

# **Characterization of Toxicologically Relevant Compounds from Diesel Emissions: Phase II**

**INTERIM REPORT**

**TFLRF No. 372**

by

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**Southwest Research Institute**

**San Antonio, TX 78238**

Under Contract to

**U.S. Army TARDEC**

**Petroleum and Water Business Area**

**Warren, MI 48397-5000**

for

**U. S. Department of Energy**

**Office of Transportation Technologies**

**1000 Independence Avenue, SW**

**Washington, D. C. 20585**

and

**Coordinating Research Council, Inc.**

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SwRI Project No. 08-03227.09 (TARDEC Contract No. DAAE-07-99-C-L053)

SwRI Project No. 08-06673 (CRC)

**March 2004**

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Approved by:

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**Edwin C. Owens, Director  
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## EXECUTIVE SUMMARY

### **Objectives:**

- Investigate the role of oxygenated diesel fuel additives on the exhaust emissions of potentially toxicologically relevant compounds in the presence of emission control devices.
- Determine the polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of exhaust particulate matter; gaseous exhaust PAH; other toxic air pollutants collected from a diesel engine using various fuel compositions and engine operating conditions.

### **Approach:**

- A DaimlerChrysler OM611 CIDI engine was used to determine the effect of diesel fuel type on toxicologically relevant compounds from engine-out exhaust emissions.
- The engine was controlled by a SwRI Rapid Prototyping Electronic Control System (RPECS).
- The test matrix included 7 fuels operated over 4 speed/load points for Low NO<sub>x</sub> operation determination.
- Each speed/load point was devised to hold Location of Peak Pressure (LPP) and EGR, while maintaining cylinder balance within 5 % of the Indicated Mean Effective Pressure (IMEP), while maintaining 0.5% NO<sub>x</sub> index.
- Three of the speed/load points were operated with four test fuels and emission control devices, while maintaining the Location of Peak Pressure and EGR at constant values.
- Four toxic air pollutant exhaust emissions were measured at three sample locations.
- Twelve gaseous PAH compounds were measured.
- Seventeen PAH compounds were determined from the soluble organic fraction of the exhaust particulate matter at two sample locations.

### **Accomplishments:**

- All fuel tests were completed in triplicate for 3 modes: engine out, oxidation catalyst out and catalyzed DPF out.
- Oxygenate-containing fuel and Fischer-Tropsch fuel produced the lowest overall toxic air pollutant and PAH exhaust emissions.

### **Future Directions:**

In a follow-on phase, similar investigations will be conducted using an engine with exhaust emission control devices and evaluating transient cold-start effects.

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## SYMBOLS AND ABBREVIATIONS

ADMM15	Blend of 15% v DMM in ALS fuel
ALS	Alternative Low Sulfur
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
ATDC	After Top Dead Center
bhp	Brake Horse Power
BMEP	Brake Mean Effective Pressure
BSFC	Brake Specific Fuel Consumption
CARB	California Reference Fuel
CIDI	Compression Ignition, Direct Injection
CO	Carbon Monoxide
CO <sub>2</sub>	Carbon Dioxide
COTR	Contracting Officer's Technical Representative
DF-2	EPA Certification Grade Diesel Fuel
DMM	Dimethoxymethane
DNPH	Dinitrophenylhydrazine
DOE	Department of Energy
DPF	Diesel Particulate Filter
EGR	Exhaust Gas Recirculation
FT-100	Neat Fischer-Tropsch Fuel
HC	Hydrocarbon
IMEP	Indicated Mean Effective Pressure
LPP	Location of Peak Pressure
NO <sub>x</sub>	Nitrogen Oxides
PAH	Polycyclic aromatic hydrocarbon
PM	Particulate Matter
PNGV	Partnership for a New Generation of Vehicles
RPECS	SwRI Rapid Prototyping Electronic Control System
RPM	Revolutions per Minute
SOF	Soluble Organic Fraction
SwRI	Southwest Research Institute
TARDEC	Tank-Automotive Research Development and Engineering Center
TFLRF	U.S. Army TARDEC Fuels and Lubricants Research Facility

## 1.0 INTRODUCTION

The control of NO<sub>x</sub> emissions is the greatest technical challenge in meeting future emission regulations for Diesel engines in the United States. As a precursor to this work a modal analysis was performed for developing an engine control strategy to take advantage of fuel properties to minimize engine-out NO<sub>x</sub> emissions. This work focused on the use of EGR to reduce NO<sub>x</sub> while counteracting anticipated PM increases by using oxygenated fuels.

Advances in fuels, engines and emission control systems are necessary in order to achieve ever-tighter emission standards. These advances are required to enable wider applications of highly fuel-efficient diesel engines in light-duty vehicle fleets around the world.

In the search for ways to modify in-cylinder events and engine-out emissions, oxygen-containing diesel fuels, formulated by the addition of several oxygenate compounds, have been studied. Several of these oxygenate compounds have shown to potentially reduce particulate matter (PM) [1-13].

The current work is the continuation of an effort that has comprised four different phases:

1. A study to quantify engine-out emissions of potentially toxic compounds from a modern diesel engine operated with 15% dimethoxy methane in a low-sulfur diesel fuel. Five diesel fuels were examined: a low sulfur (~1 ppm) fuel, a low sulfur fuel containing 15% dimethoxy methane, a Fischer-Tropsch fuel, a California reformulated fuel, and a EPA number 2 certification fuel. It was demonstrated that, for engine-out emissions of toxicologically important compounds, the use of 15 % dimethoxy methane in a low-sulfur diesel fuel (4.7%w of oxygen) or a 100% Fischer-Tropsch fuel lowered emissions from a modern light-duty diesel engine while pilot injection raised emissions [1-3].
2. A literature review was conducted to identify potential oxygenates for blending into diesel fuels. As many as 71 oxygenates were identified for the initial screening process. Based on a set of physical and chemical properties, a screening methodology was

developed to select the 8 best of these 71 oxygenates possible for engine testing. Preliminary screening reduced the field to 43 candidate oxygenates. Properties not found in the literature such as solubility and corrosivity were evaluated using bench tests. Further screening produced the eight oxygenates found to be satisfactory for engine testing [4].

3. A further study was performed to select the most promising of these 8 oxygenates as blending components in diesel fuel for advanced engine testing. A fuel matrix was designed to consider the effect of molecular structure and boiling point on the ability of oxygenates to reduce engine-out exhaust emissions from a modern diesel engine. Nine test fuels including one low-sulfur (~1 ppm), low aromatic hydrocracked base fuel and eight oxygenate-base fuel blends were utilized. All oxygenated fuels were formulated to contain 7% wt. of oxygen. Based on Total PM emissions and the previous screening process, tripropylene glycol monomethyl ether and dibutyl maleate were identified as the most promising candidate oxygenate compounds for future engine testing [6].
4. A study performing a modal analysis for developing an engine control strategy to take advantage of fuel properties in order to minimize engine-out NO<sub>x</sub> emissions. This study focused on the PM reducing capabilities of tripropylene glycol monomethyl ether and dibutyl maleate; the two oxygenated compounds selected previously [5,6]. It was possible to decrease mode-weighted NO<sub>x</sub> emissions compared to the OEM calibration – generally with corresponding increases in other emissions. These emissions increases could be partially overcome with the use of oxygenated fuels. However, increases in fuel consumption and losses in engine boost proved to be more significant in limiting practical NO<sub>x</sub> control than the emission reduction benefits from fuel composition changes [14].

## 2.0 BACKGROUND

This report presents follow-on work to the Phase I PM Analysis Project that was entitled, “Characterization of Toxicologically Relevant Compounds from Diesel Emissions”. During 2000 the Department of Energy and the Auto-Energy Ad-Hoc Fuels Group, jointly undertook an assessment of the role that selected fuel changes would have on the engine-out emissions of a subset of potentially toxicologically relevant compounds. This was part of an overall study that examined the effects of alternative diesel fuel formulations on exhaust emissions in an advanced CIDI engine.

In the Phase I PM Analysis Project, a DaimlerChrysler OM611 CIDI engine, controlled by a SwRI Rapid Prototyping Electronic Control System (RPECS), was operated over five steady-state speed/load points. At each speed/load point, injection timing was adjusted for each fuel to place the peak cylinder pressure of combustion at 7° ATDC, while adjusting individual fuel volume injected within each cylinder in order to maintain the Indicated Mean Effective Pressure (IMEP) of each cylinder to within 5% of the mean, with pilot fuel injection disabled. The test matrix included five fuels, including one oxygenate blend [Table 1]. Regulated gaseous exhaust emissions and particulate matter (PM) were measured. In addition, four gaseous toxic air pollutants exhaust emissions and eleven gaseous PAH compounds were measured. Seventeen PAH compounds were determined from the soluble organic fraction of the exhaust particulate matter.

<b>Table 1. PM Analysis Phase I Test Fuels</b>						
<b>Fuel (Code)</b>	<b>H wt %</b>	<b>C wt %</b>	<b>O wt %</b>	<b>Cetane Number</b>	<b>Sulfur, ppm</b>	<b>Aromatic s, wt%</b>
California Reference Diesel (CA)	13.4	86.4	0.2	45	176	18.9
Low-Sulfur Diesel (ALS)	14.4	85.6	0.0	63	1	9.0
Fischer-Tropsch Diesel (FT-100)	15.1	84.8	0.1	84	0	0.2
Oxygenate: 15% Dimethy-oxymethane in ALS (ADMM15)	13.7	81.6	4.7	59	< 2	8.2
EPA 2D Certification Fuel (DF-2)	13.0	86.7	0.3	44	337	30.3

The fuel rank order for exhaust emissions can be summarized as follows:

- PM emissions were lowest for ADMM15 and FT-100 and highest of DF-2
- NO<sub>x</sub> emissions were lowest for FT-100, ADMM15 was in the middle, and DF-2 emissions were the highest
- Gaseous toxic air pollutants emissions were the lowest for FT-100 and ADMM15, and highest for DF-2
- Both soluble and gas phase PAH emissions were the lowest for FT-100 and ADMM15, and DF-2 fuel emitted the highest amount

The study provided a large volume of data, and one should refer to the report [15] for details of the measurements and the statistical analysis. However, there were clear, statistically significant differences among the fuels:

- ADMM15 or FT-100 had the lowest overall weighted average emission response of the test fuels
- ADMM15 fuel was statistically the same as FT-100 fuel for toxic air pollutants, PM, and PAH emissions

The PM Analysis Phase II project is part of an overall study that examines the effect of oxygenated compounds in diesel fuel on the emissions of particulate matter, oxides of nitrogen, and fuel economy when emission control devices are used. The project will focus on the chemical characterization of emissions of compounds with known or suspected toxicological properties while minimizing engine-out emissions of NO<sub>x</sub>. Exhaust emissions of compounds that are measured after emission control devices will be compared to the engine-out emissions to better understand the effects of emission control devices and alternative fuels.

### **3.0 OBJECTIVE**

The overall objective of this project was to better understand the role of fuels and emission control devices on the exhaust emissions of a subset of potentially toxicologically relevant compounds. The three objectives of this program were to measure the following pollutants collected from diesel engines under a matrix of engine and fuel conditions that minimize engine-out emissions of NO<sub>x</sub>:

1. Polycyclic aromatic hydrocarbon (PAH) content of organic solvent extracts of particulate matter
2. Gas phase polycyclic aromatic hydrocarbons
3. Gaseous toxic air pollutants (formaldehyde, acetaldehyde, benzene and 1,3-butadiene)

These first two measurements were made on engine out exhaust emissions, after an oxidation catalyst, and after a diesel particulate filter. Polycyclic aromatic hydrocarbon (PAH) measurements of organic solvent extracts of particulate matter were not attempted because of the very low amounts of particulate matter emitted after the particulate filter trap.

An additional objective is to determine if the benefits of oxygenated diesel fuels on exhaust toxicity are still valid for low NO<sub>x</sub> operating conditions, and when exposed to emission control devices.

### **4.0 TECHNICAL APPROACH**

#### **4.1 Test Engine**

The engine used in this investigation was a DaimlerChrysler OM611. The OM611 engine is a 2.2L, direct-injection, compression-ignition, with a Bosch, high-pressure, common-rail, fuel-injection system. The OM611 engine is turbocharged with wastegate

control and utilizes an intercooler. The engine design closely matches the specifications of the partnership for a new generation vehicle (PNGV) target compression-ignition direct-injection (CIDI) engine. Characteristics of the OM611 engine are presented in Table 2.

<b>Table 2. OM611 Engine Performance Characteristics</b>	
Displacement	2151 cm <sup>3</sup>
Maximum Power	92 kW at 4200 RPM
Maximum Torque	300 N-m at 1800 - 2600 RPM
Maximum BMEP	17.5 bar
Compression Ratio	19:1
Minimum Specific Fuel Consumption	203 g/kW-hr

Besides the electronically controlled common rail fuel injection system, the OM611 engine has several other unique features that affect combustion. The engine has two intake ports, one helical for swirl, and one high flow port. The high flow port also contains an Intake Runner Valve (IRV), which is used to shut the port off at low speeds and light loads. This allows for variable swirl in the engine for improving light load exhaust emissions.

The OM611 engine also utilizes variable Exhaust Gas Recirculation (EGR). The EGR is controlled with pulse width modulation of an EGR valve and intake damper, and is referenced to the engine mass airflow sensor. The high EGR region is from idle to approximately 50% speed and 50 % load. The hot EGR passes through a cooling passage integral with the cylinder head, then on to the intake manifold via the EGR valve.

A feature of the OM611 engine, used for controlling both exhaust and noise emissions is the employment of pilot fuel injection. The pilot fuel injection results in a slower start of combustion, which reduces noise levels and may reduce Oxides of Nitrogen emissions. Pilot fuel injection is disabled when the engine is operating above 3000 RPM and 50 % load.



## **4.2 Engine Setup**

### **4.2.1 Test Cell**

The OM611 engine was installed in a test cell supplied with conditioned air and attached to an eddy current absorption dynamometer as shown in Figure 2. The engine load was monitored with an electronic load cell. The engine speed was monitored using a 60-tooth gear and a frequency to voltage converter. The fuel system included a constant level day tank, and a Micro-Motion mass flow sensor. Intake air mass flow was measured according to SAE J244 using a Merriam Laminar Flow Element.

The engine was fitted with a gaseous exhaust sample probe and a heated sample line to the emission bench. An exhaust particulate sampling probe was inserted into the exhaust and connected to a 203 mm diameter dilution tunnel. Exhaust dilution ratio was monitored using carbon dioxide tracer. Dilution tunnel sample zone temperature was maintained below 125°F by splitting the engine exhaust.

### **4.2.2 Electronic Engine Control**

The stock engine control unit (ECU) was replaced with the SwRI developed Rapid Prototyping Electronic Control System (RPECS). The RPECS system is a PC-based tool (both hardware and software) that is used for real-time embedded powertrain control system development. The procedure for installing the RPECS hardware involved intercepting and mapping the signals from the stock engine controller. The engine calibration tables and control signals are then duplicated with the RPECS hardware/software in order to control the engine. The operating parameters of interest will be adjusted through changes to the calibration tables in RPECS.

The RPECS has been configured to allow control of the common rail fuel injection system, and intake manifold conditions. The items controllable by RPECS as presently configured are shown in Table 3.

Table 3. RPECS Controlled Engine Parameters				
Common Rail Fuel Injection				
Fuel Injection	Cylinder 1	Cylinder 2	Cylinder 3	Cylinder 4
Timing	Individual	Individual	Individual	Individual
Duration	Individual	Individual	Individual	Individual
ON/OFF	Individual	Individual	Individual	Individual
Pilot ON/OFF	Global			
Pilot-to-Main Timing	Global			
Pilot Duration	Individual	Individual	Individual	Individual
Pilot/Main Duration Ratio	Individual	Individual	Individual	Individual
Rail Pressure	Global			
Intake Manifold				
Boost - PWM Variable				
Intake Runner Valve - ON/OFF				
EGR - PWM Variable, Intake Mass Air Flow feedback, measured by intake/exhaust CO <sub>2</sub>				

The RPECS uses pulse width modulation (PWM) for closed-loop control of EGR, manifold pressure, and the common rail fuel injection pressure. The feedback for the EGR control loop is the engine mass airflow sensor. The manifold pressure sensor provides feedback for RPECS, with the turbocharger wastegate utilized as the control element. The common rail fuel pressure is controlled with a PWM fuel pressure vent, with feedback from a 1500 bar rail pressure sensor.

The RPECS has an eight-channel timer board that synchronizes with the engine crankshaft and camshaft pulses for activation of the fuel injectors. Each cylinder of the engine utilizes two timer channels, one for the pilot fuel injection event and one for the main fuel injection event. The fuel injectors are powered by peak-and-hold drivers, which allow variation of timing and duration of both pilot and main fuel injection. Additional fuel injection control features include individual cylinder control of pilot and main fuel injection events and pilot/main fuel injection ratio control.

One-dimensional tables, one for speed and one for load, were programmed into RPECS so that the engine operating conditions could be consistently repeated. The RPECS was operated in a closed-loop torque control mode. In closed-loop torque control RPECS adjusts fuel injection quantity to attain the set point torque value from the dynamometer electronic load cell feedback. In closed-loop torque mode the engine speed is controlled by an eddy-current dynamometer controller. All fueling variations to maintain the

closed-loop torque value were made by adjustments to the main fuel injection pulse, leaving the pilot fuel injection pulse constant.

#### **4.2.3 Cylinder Pressure Transducers**

Program modifications were made to the RPECS to allow individual cylinder fuel injection timing and quantity control. Pressure transducer adapters were machined to fit in the cylinder head via the glow-plug passages. Kistler 6052A transducers were mounted in the adapters. All cylinder pressure transducers were calibrated, and connected to a DSP Technologies high-speed data acquisition system for combustion analysis and cylinder balance. The DSP was clocked with a 720 pulse/revolution shaft encoder.

#### **4.2.4 Emission Control Devices**

The test engine was fitted with a close coupled oxidation catalyst and a catalyzed diesel particulate filter. A MECA representative to the Ad-Hoc Steering Committee has specified the emission control devices.

The oxidation catalyst formulation is from a mature family of oxidation catalysts targeting European emissions standards. Improvements include emphasis on low temperature CO oxidation for targeting start up CO emissions on a modern common rail DI passenger vehicle on the European light-duty cycle. The loading of 70 g/cu ft is in the middle of the range that might be used, dependent on the actual application temperatures, and should be appropriate for a close-coupled, relatively "large" catalyst on a Euro IV vehicle application. The test catalyst is probably not large enough to be the only catalyst on such a vehicle, but would be combined with a larger, lower loading underfloor catalyst of similar washcoat technology. The catalyst may also be part of an Euro IV system that includes a CDPF. The catalyst has not been optimized for the competing needs of low light off temperature and high resistance to thermal aging during oxidation of large amounts HC and CO from late-cycle in-cylinder post-injection.

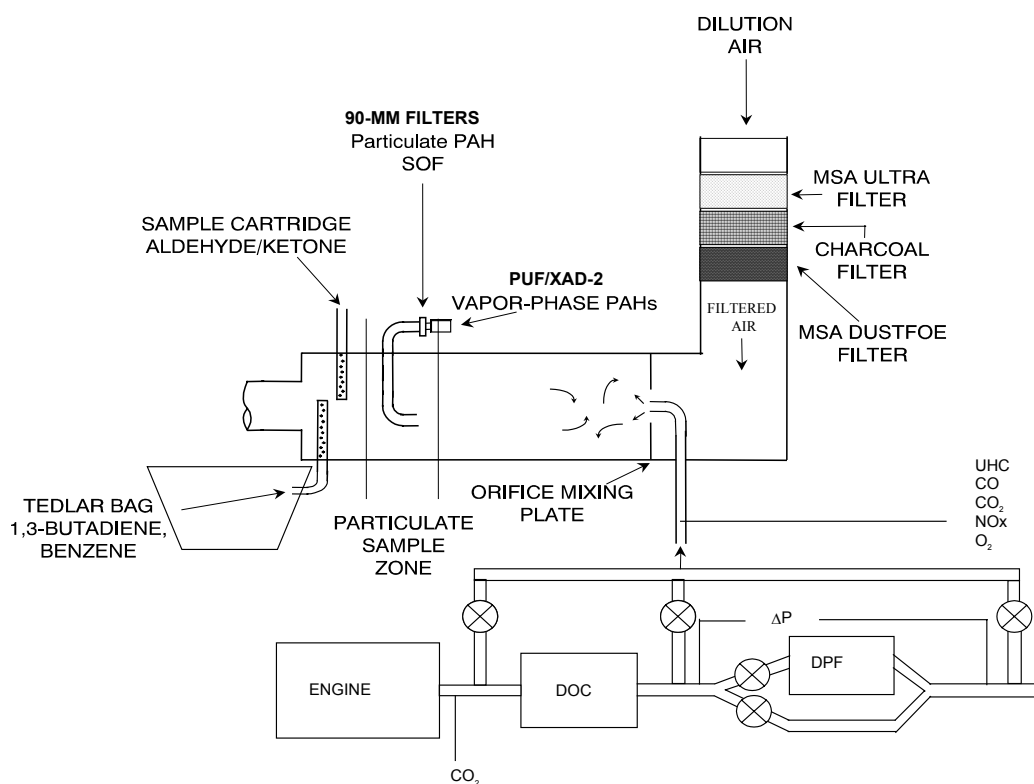
The catalyst formulation on the CDPF is less mature, but similar to that showing success in prototype form in heavy-duty retrofit applications. The washcoat loading is very low to minimize the flow restriction added to the base filter. The platinum loading is in the middle of the range that seems to be proposed for such devices, but is in a relatively high concentration in the relatively low mass washcoat. As a result of the low washcoat loading and the filter geometry, the microscopic surface area available to gasses is limited compared to an oxidation catalyst of similar size, so it is not expected to give as good gaseous HC and CO performance as a second underfloor catalyst for a non-filter Euro IV application might.

The combination of the above devices may be adequate for a given Euro IV application, but does not represent the greatest practical gaseous oxidation potential due to the limited size of the close coupled catalyst and the limited washcoat / surface area of the filter.

### **4.3 Exhaust Emissions Measurement**

The OM611 engine was instrumented for the exhaust species shown in Table 4 and as diagramed in Figure 1. The gaseous and particulate emissions were drawn from the raw exhaust, with sample probes located (when practical) approximately three pipe diameters downstream of the turbocharger or emission control device outlet. The gaseous exhaust sampling probe was located upstream of the back pressure regulating butterfly. The backpressure regulating butterfly was locked in the position that produced 11 in/hg backpressure at rated speed and load. The gaseous emissions sampling was performed in accordance with the guidelines outlined in 40 CFR Part 86, Subpart D. The OM611 engine exhaust was coupled to the house exhaust system and a Constant Volume Sampling (CVS) system. The CVS system consists of a 203 mm dilution tunnel, with a Variable speed Roots type blower. In order to attain a 125°F filter face temperature with the CVS system, the engine exhaust was split between the house exhaust and the dilution tunnel. The dilution tunnel sample zone temperatures were verified at each of the test modes.

Table 4. Analytical Instrumentation	
Constituent	Analysis Method
Total Hydrocarbon	Heated Flame Ionization Detector
Carbon Monoxide	Non-Dispersive Infrared Analysis
Carbon Dioxide	Non-Dispersive Infrared Analysis
Oxides of Nitrogen	Chemiluminescent Analysis
Particulate Matter	Gravimetric, CVS, CO <sub>2</sub> tracer
Soluble Organic Fraction of PM	Gravimetric, Soxhlet Extraction Toluene/Ethanol
Benzene	Gas Chromatography
1,3-Butadiene	Gas Chromatography
Formaldehyde	DNPH Adsorbent/High Pressure Liquid Chromatography
Acetaldehyde	DNPH Adsorbent/High Pressure Liquid Chromatography
Polycyclic Aromatic Hydrocarbons	Gas Chromatography/Mass Spectroscopy/Selected Ion Monitoring



**Figure 1. Schematic Representation of Emissions Sampling System**

A carbon dioxide tracer technique was utilized to determine the dilution ratio in the CVS system. The particulate matter sampling procedures were performed in accordance with the guidelines established in 40 CFR Part 86, Subpart N. A polyurethane foam and XAD-2 resin trap were utilized for sampling gas phase PAH compounds. Soluble phase PAH compounds were extracted from 90 mm filters. Benzene and 1,3-butadiene were

collected in a sample bag from the dilution tunnel sample zone. Formaldehyde and acetaldehyde were trapped on a DNPH adsorbent cartridge from the dilution tunnel sample zone.

#### **4.3.1 Gaseous Emissions Analyses**

The following three groups of gaseous engine out exhaust emissions were determined for each test point, i.e. engine mode, fuel, and sample location combination.

##### **4.3.1.1 Typical Exhaust Gases**

The following species concentrations were measured utilizing the instrumentation shown in Table 4:

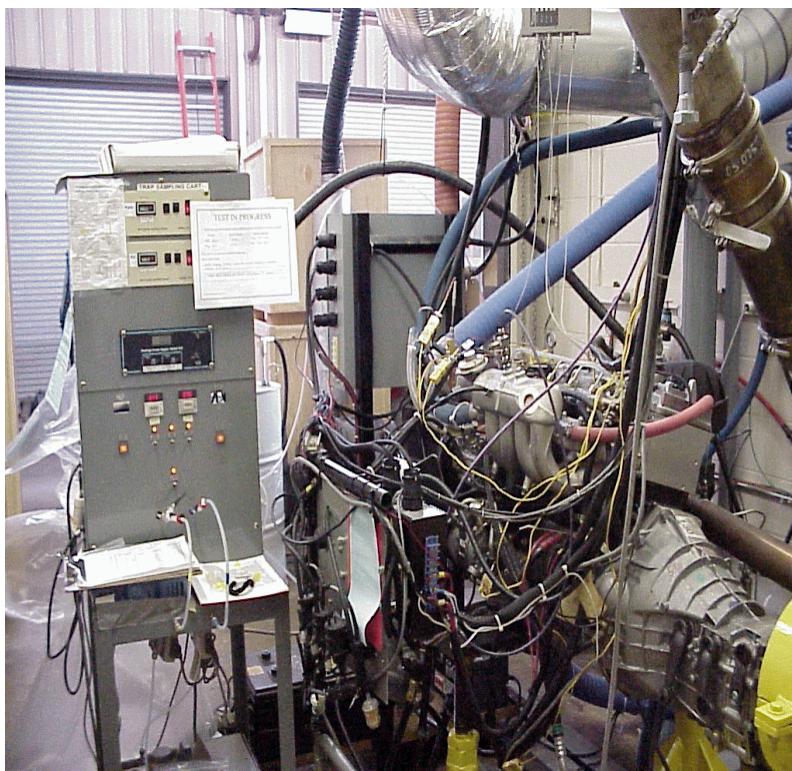
- hydrocarbons (HC)
- carbon monoxide (CO)
- carbon dioxide (CO<sub>2</sub>)
- oxides of nitrogen (NO/NO<sub>x</sub>)
- oxygen (O<sub>2</sub>)

##### **4.3.1.2 Toxic Air Pollutants Cited in the Clean Air Act**

A sample cart, as seen in Figures 2 and 3, was configured and placed in the test cell near the engine and exhaust dilution tunnel. This cart was arranged so that one technician could effectively collect bag samples and cartridge samples simultaneously. The cart was utilized for sampling the following four Clean Air Act toxic air pollutants:

- benzene
- 1,3-butadiene
- formaldehyde
- acetaldehyde

The front of the cart was used to control and monitor the cartridge sampling for formaldehyde and acetaldehyde while the back of the cart supported the pumps and metering valves for collecting the bag samples for benzene and 1,3-butadiene analyses.



**Figure 2. Gas Sampling Cart – Front**



**Figure 3. Gas Sampling Cart Rear**

#### 4.3.1.2.1 Benzene and 1,3-Butadiene

Exhaust samples for benzene and 1,3-butadiene determination were taken in Tedlar7 bags via a diaphragm vacuum pump from a dilution tunnel through an unheated 1/4" Teflon tube. A corresponding background air sample was taken from the ambient air. The collected samples were transported to the SwRI Department of Emissions Research (DER) for analysis. These two toxic air pollutant compounds were analyzed using two different gas chromatographs (GC) as described in Table 5. The two GCs were configured and operated according to the CRC Auto-Oil Phase II Air Quality Improvement Research Program guidelines. These instruments were calibrated with CRC/NIST gas mixtures according to DER Standard Operating Procedures. Detection limits for the GCs are on the order of 10 parts per billion.

<b>Table 5. Gas Chromatographic Analysis Parameters</b>		
	<b>1,3-Butadiene</b>	<b>Benzene</b>
<b>Gas Chromatograph</b>	Hewlett- Packard 5890-II	Hewlett- Packard 6890
<b>Injector</b>	10 port gas sampling valve w/ 5 mL sample loop	10 port gas sampling valve w/ 5 ml sample loop
<b>Detector</b>	hydrogen flame ionization	hydrogen flame ionization
<b>Column/s</b>	DB-Wax, 15 meter x 0.53mm, 1.0 film, J&W Scientific, Alumina PLOT/KCL, 50meter x 0.53mm, 10 µm film, Chrompack, International	pre-column: 2 meter of 0.25 mm I.D. deactivated fused silica  Analytical column: 30 m x 0.25 mm DB-5, 0.25 µm film thickness

#### 4.3.1.2.2 Formaldehyde and Acetaldehyde

To collect the aldehydes, a metered volume of the dilute exhaust was transferred with a diaphragm vacuum pump from the dilution tunnel through a heated sample transfer line and heated particulate filter, both maintained at 375°F and finally through a cartridge containing silica impregnated with 2,4-dinitrophenylhydrazine (DNPH), Figure 4. A metered volume of the background air was pulled through another cartridge. A Hastings model HFC-202D mass flow meter was used to measure the volume of gases sampled. The engine control computer recorded air temperature and barometric pressure. Any aldehyde or ketone present in the sampled gas reacted quickly with the DNPH to form a stable derivative (R-CHO phenylhydrozone). These derivatives were extracted from the trap with ultra-pure acetonitrile. Analysis of the extracted samples and backgrounds were performed using a high performance liquid chromatograph (HPLC), pumping a ternary



solvent gradient of water, methanol, and acetonitrile through an ultra-violet (UV) spectroscopic detector. The instrument was calibrated using purified aldehyde derivatives according to the DER Standard Operating Procedures. The detection limit for this instrument is on the order of 0.005 ppm aldehyde in dilute exhaust.



**Figure 4. Sample Cartridges**

The collection of optimum sample volumes during the engine test modes required precise timing of starting and stopping pumps and opening and closing valves by the cart operator. Appendix A describes the sequence of these events. Revision to the first sequence was determined necessary when HPLC analyses indicated overloading or breakthrough of the DNPH aldehyde cartridges. Background cartridge samples were a composite of one entire day of sampling.

#### 4.3.1.3 Gaseous PAH Compounds

The gaseous phase (PUF/XAD-2 trap) samples are Soxhlet extracted with methylene chloride for 18 hours. At the beginning of the extraction, 20 uL of a PAH surrogate spiking solution containing three deuterated PAH [benzo(b)fluoranthene-d12, benzo(a)anthracene-d12, and dibenz(a,h)anthracene-d14 at 50 nanograms each] is spiked into the sample. Sample extracts are then concentrated to a known interim volume (usually 20 mL) and split 50:50 with one portion serving as a reserve. The remaining portion of each sample extract is then solvent exchanged into hexane. A cleanup procedure that consists of an acid wash and liquid chromatography is then applied. The acid used is a diluted sulfuric acid. The chromatography is performed on a silica gel column that would separate fuel and oil from the PAHs. The sample extracts were in hexane, transferred onto the Si column, the column flushed with hexane (to remove the fuel and oil), and the PAHs were then eluted out of the column by using a DCM/pentane solvent system. The sample extracts, after the cleanup, were blown down to a final volume of 500 microliters (uL). An internal standard mixture containing deuterated PAH is added to these extracts prior to GC/MS/SIM (selected ion monitoring) analysis. Two or three characteristic ions of each PAH are monitored. A PAH calibration curve consisted of at least 5 points is obtained prior to the sample analysis. A solvent or lab blank is analyzed immediately after the last calibration standard analysis to ensure no significant carryover occurs on the instrument. The PAH are analyzed in the positive ion electron impact (PI/EI) mode. Separate GC/MS/SIM analyses are necessary to acquire the PAH data.

The estimated detection limits (DLs) are 10.0 nanogram (total) per PAH per sample. This is based on the lowest calibration standard of 0.01 ng/uL/PAH with a 500 uL final volume with a split factor of 2 for the reserved portions of the sample extracts. Note, different target compounds behave differently on the instrument and, therefore, exert different final DLs. The DLs given here should be considered as estimated values. There are other factors such as massive interference, and/or split samples for other analyses that will inevitably increase the DLs. A PUF/XAD-2 filter blank was extracted with each set

of engine PUF/XAD-2 filters. The PUF/XAD-2 blank was analyzed to determine the PAH background from the media. Additionally a PUF/XAD-2 tunnel blank was analyzed to determine the PAH background from the test cell, dilution tunnel, and sample system. The tunnel blanks were drawn for four hours; the background values that are reported in Table 6 have been adjusted to represent the 30-minute sample time that was used during engine testing. Included in Table 6 is the reported detection limits for each gaseous phase PAH compound. The gaseous phase PAH compounds were analyzed using a high-resolution gas chromatograph with a 1.0 atomic mass unit (AMU) low-resolution mass spectrographic detector. There were not any non-detects for gaseous phase PAH compounds during testing.

<b>Table 6. Gaseous Phase PAH Backgrounds and Detection Limits</b>			
<b>COMPOUND</b>	<b>Average PUF/XAD-2 Filter Blank</b>	<b>Average PUF/XAD-2 Tunnel Blank</b>	<b>PUF/XAD-2 Extract HRGC/LRMS(1 AMU) Detection Limit</b>
	<b>ng/sample</b>	<b>ng/sample</b>	<b>ng/sample</b>
Naphthalene	369	2227	10
2-Methylnaphthalene	181	945	10
1-Methylnaphthalene	132	572	10
Biphenyl			10
2,6-Dimethylnaphthalene	105	618	10
Acenaphthylene	102	113	10
Acenaphthene	105	114	10
Fluorene	113	192	10
Phenanthrene	128	597	10
Anthracene	112	22	10
Fluoranthene	104	22	10
Pyrene	101	22	10

#### **4.3.2 Exhaust Particulate Matter Analyses**

The soluble organic fraction of diesel exhaust particulate collected on 90 mm Pallflex filters was removed from the particulate using a Soxhlet extraction system. The extraction solvent was 30 percent toluene/ 70 percent ethanol by volume. Twenty microliters of a PAH surrogate spiking solution, containing three deuterated PAH (benzo(b)fluoranthene-d12, benzo(a)anthracene-d12, and dibenzo(a,h)anthracene-d14, at 50 nanograms each) was syringed onto each filter prior to solvent extraction to determine

the PAH extraction efficiency. This Soxhlet extraction method is similar to washing the filter with approximately five gallons of solvent. The percent mass extracted from the diesel particulate on the filter is determined by weight loss, usually in milligram quantities, after solvent extraction and drying.

The exhaust particulates were analyzed for Soluble Organic Fractions (SOF) and specific PAH compounds following Modified EPA Protocol 8270C. The particulate (filter) samples are analyzed the same way as described above for the PUF/XAD-2 samples except the solvent used for the PM filter extraction is ethanol/toluene (30/70 v/v).

Three 90 mm Pallflex filter blanks were extracted and analyzed to determine the PAH background from the media. Additionally, a 90 mm Pallflex tunnel blank was analyzed to determine the PAH background from the test cell, dilution tunnel, and sample system. The tunnel blanks were drawn for four hours; the background values that are reported in Table 6 have been adjusted to reflect the 30-minute sample time that was used during engine testing. Included in Table 7 is the reported detection limits for each gaseous phase PAH compound for two analytical instruments. Due to low levels of contamination, the filter and tunnel blanks had lower detection limits than the SOF extracts. The particulate matter PAH compounds were initially analyzed using a high-resolution gas chromatograph with a 1.0 atomic mass unit (AMU) low-resolution mass spectrographic detector. Depending on the engine-operating mode and test fuel utilized, there were non-detect values for several key PAH compounds. Primarily, the non-detects were reported due to interference from other organic compounds around the molecular weight of the compound of interest. For the higher molecular weight PAH compound shown in Table 7, a high-resolution gas chromatograph with a 0.01 atomic mass unit (AMU) high-resolution mass spectrographic detector was used for selected test runs.

Table 7. Particulate Matter PAH Backgrounds and Detection Limits						
COMPOUND	Average Pallflex 90mm Filter Blank		Average Pallflex 90mm Tunnel Blank		SOF Extract HRGC/LRMS(1AMU) Average Detection Limit	SOF Extract HRGC/HRMS(0.01AMU) Average Detection Limit
	ng/sample	DL	ng/sample	DL	ng/sample	ng/sample
Naphthalene	543	3	245	4	10	
Acenaphthylene	9	3	8	4	10	
Acenaphthene	74	3	37	4	10	
Fluorene	120	3	62	4	10	
Phenanthrene	665	3	370	4	10	
Anthracene	63	3	16	4	10	
Fluoranthene	89	3	85	4	10	
Pyrene	41	3	67	4	10	
Benzo[a]anthracene	1	3	2	4	10	
Chrysene	3	3	5	4	10	
Benzo[b]fluoranthene	1	3	6	4	10	
Benzo[k]fluoranthene	1	3	4	4	10	
Benzo[e]pyrene	1	3	3	4	10	
Benzo[a]pyrene	0.6	3	1	4	10	0.1
Indeno(1,2,3-cd)pyrene	ND	3	2	4	10	0.1
Dibenzo[a,h]anthracene	ND	3	1	4	10	0.25
Benzo[ghi]perylene	0.9	3	3	4	10	0.1

#### 4.4 Measured Quantities and Accuracy

Table 8 shows the estimated accuracy of the engine and emission measurements.

Table 8. Measured Quantities			
Quantity	Description	Unit	Accuracy
Engine Speed		rpm	+/- 4.2
Engine Load		ft-lb	+/- 2.3
Fuel Flow		lb/hr	+/- 5%
Temp. Coolant In		°F	+/- 4
Temp. Coolant Out		°F	+/- 4
Temp. Oil		°F	+/- 4
Temp. Intake Air		°F	+/- 4
Temp. Fuel		°F	+/- 4
Temp. Exhaust		°F	+/- 25
Temp. Intercooler In		°F	+/- 4
Temp. Intercooler Out		°F	+/- 4
Temp. Air Dewpoint		°F	+/- 4
Pres. Ambient		"hg	+/- 1%
Pres. Exh. Restriction		"hg	+/- 1%
Pres. Boost Pre-Intercooler		"hg	+/- 1%
Pres. Boost Post-Intercooler		"hg	+/- 1%
Carbon Monoxide	CO	g/kW-hr	+/- 15%
Hydrocarbon	HC	g/kW-hr	+/- 20%
Nitric Oxides	NO <sub>x</sub>	g/kW-hr	+/- 10%
Carbon Dioxide	CO <sub>2</sub>	g/kW-hr	+/- 10%
Particulate (Total)	PM	g/kW-hr	+/- 20%

## 4.5 Fuels

The proposed test fuel matrix was designed by the Ad-Hoc CIDI Fuels Steering Committee, which includes the Department of Energy (DOE). The dimethoxymethane used to add oxygen to the fuel in previous DOE studies [1-3,16] was replaced with tripropylene glycol monomethyl ether and dibutyl maleate, as previously discussed. The fuel matrix included the following fuels with their selected properties shown in Table 9:

<b>Table 9. Fuels and Selected Fuel Properties</b>								
<b>Fuel</b>	<b>ASTM Method</b>							
	<b>D 5291</b>		<b>Diff.*</b>	<b>D 613</b>	<b>D 5453</b>	<b>D 5186</b>	<b>D 86</b>	<b>D 240</b>
	<b>H, wt %</b>	<b>C, wt %</b>	<b>O, wt %</b>	<b>Cetane Number</b>	<b>Sulfur, ppm</b>	<b>Aromatics, wt%</b>	<b>T90, °C</b>	<b>Net Heating value, MJ/kg</b>
1. DECSE	13.4	86.3	0.3	44.8	3.1	27.0	314	43.1
2. ECD-1	13.5	86.2	0.3	52.8	11	21.7	326	41.7
3. BP15	13.4	86.4	0.2	49.7	14.8	27.2	321	42.9
4. ECD-1 + TPGME for 7%(w/w) O <sub>2</sub>	12.9	80.0	7.1	52.0	8.5	17.0**	319	38.7
5. Fischer-Tropsch	15.1	84.8	0.1	84	<1	0.20	325	43.2
6. BP15 + TPGME for 7%(w/w) O <sub>2</sub>	12.8	80.3	6.9	48.4	11	21.2**	320	39.1
7. BP15 + DBM for 7%(w/w) O <sub>2</sub>	12.2	80.6	7.2	45.9	25.5	20.6**	319	38.9
*Calculated by Difference;** Estimated from blend component values								

1. DECSE fuel, low sulfur (3 ppm) diesel fuel used in the DOE DECSE program. This fuel was blended from narrow-cut refinery streams to produce a very low sulfur fuel that is representative of 49-state No. 2 diesel fuel in all other ASTM D975 performance properties [17].
2. ECD-1, Environmentally Clean Diesel, a low sulfur California-type diesel fuel.
3. BP15, a 15 ppm sulfur diesel fuel prepared by processing straight-run distillate stocks through a commercial, single-stage hydrotreater employing a high-activity catalyst at maximum severity. This fuel was prepared in a commercial refinery unit (not a pilot plant), but cracked stocks were excluded from the feed because the specification sulfur level could not have been achieved with their inclusion. Year 2007 actual

production will likely employ more advanced processing to allow the inclusion of cracked stocks.

4. A fuel blend of ECD-1 low sulfur California-type diesel fuel with tripropylene glycol monomethyl ether added to achieve 7-weight percent oxygen.
5. FT100, neat Fischer-Tropsch fuel.
6. A fuel blend of BP15 low sulfur diesel fuel with tripropylene glycol monomethyl ether added to achieve 7-weight percent oxygen.
7. A fuel blend of BP15 low sulfur diesel fuel with dibutyl maleate added to achieve 7-weight percent oxygen.

#### **4.6 Lubricant**

The same SAE 5W30 (viscosity grade) synthetic lubricant in the Phase I project was used in this project. The synthetic oil contains fewer volatile fractions than a petroleum-based lubricant of the same viscosity grade. Using the synthetic oil will minimize oil contribution to exhaust particulate. Oil changes after each fuel evaluation were made to minimize the engine oil contaminant contribution to exhaust particulate.

### **5.0 DESIGN OF EXPERIMENT**

#### **5.1 Steady-State Operating Conditions**

The engine was installed in a steady-state test cell. The engine was supplied with conditioned intake air, controlled to EPA intake conditions. EPA intake air conditions are shown in Table 10.

<b>Table 10. EPA Intake Air Conditions</b>		
<b>Parameter</b>	<b>Set Point</b>	<b>Tolerance</b>
Intake Pressure	100 kPa	±1 kPa
Intake Temperature	25°C	± 2°C
Intake Dew Point	15°C	± 1°C

### 5.1.1 Modes

Three modes of steady-state operation (speed/load points) were eventually included in the investigations included in this report. Due to testing difficulties and other constraints, one mode of operation was eliminated from the test matrix. Table 11 shows the engine steady-state test points, while Figure 5 shows various operating points that had been considered in relation to the baseline torque curve.

Table 11. Steady-State Test Points			
Mode	BMEP, bar	RPM	MB Equiv. Torque, ft-lb <sub>r</sub>
M22	1.0	1500	12.0
M11	2.62	1500	33.1
M6	4.20	2300	53.0

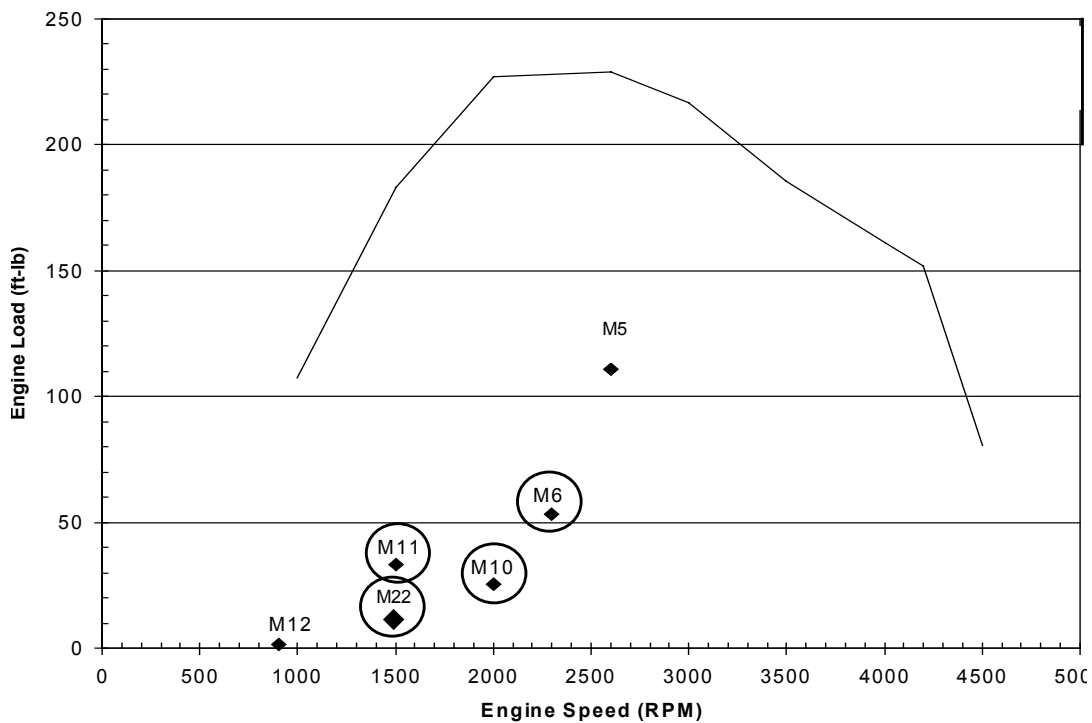


Figure 5. Speed/Load Points for Engine Operating Modes



### **5.1.2 Low NO<sub>x</sub> Emission Engine Operation**

Originally four engine operation modes were scheduled to be evaluated: Modes 6, 10, 11, and 12. The specific engine operating parameters, such as injection timing for location of peak pressure, and percentage EGR were investigated. The goal was to use specific engine operating parameters that may be used to meet future NO<sub>x</sub> and PM emissions standards. All operating modes considered are shown in Table 12, which also includes a weighting factor for estimating (hot-start) FTP-75 drive cycle emissions based on steady-state results. [12,13]

<b>Table 12. Modal Operating Conditions</b>				
<b>Run Mode</b>	<b>BMEP, bar</b>	<b>Engine Speed, RPM</b>	<b>OM611 Equiv. Torque, ft-lbf</b>	<b>Mode Weight</b>
22	1.0	1500	12.6	400
12	0.1	900	1.3	700
11	2.62	1500	33.1	600
10	2.00	2000	25.3	200
6	4.20	2300	53.0	200
5	8.8	2600	112	75

Idle Mode 12 was removed from the test program due to its low exhaust temperature of approximately 150°C. This temperature is too low to keep an oxidation catalyst active during steady state testing. During the FTP, the oxidation catalyst would remain active at idle, because the thermal inertia of the exhaust system would carryover heat from other portions of the drive cycle. Mode 5 (2600 rpm, 8.8 bar BMEP) was briefly considered as a replacement for mode 12, but it proved more appropriate to simulate the US06 cycle than the FTP-75.

A representative from the Manufacturers of Emission Controls Association suggested that the catalyst transition temperature range, 170°C-200°C, might be more interesting for typical light-duty diesel operation. At such low temperatures, partial oxidation products may play a significant role in the future planned study of toxic air pollutants produced by

emission control equipment. Exploratory engine operations at 1250 rpm and 1500 rpm (1.0 bar-BMEP) were evaluated to obtain exhaust stack temperatures; exhaust stack temperature at the OEM calibration condition was 167°C at 1250 rpm, and 179°C at 1500 rpm. Exploratory runs at a low NO<sub>x</sub> operating condition with increased EGR and retarded timing increased the exhaust stack temperature at 1500 rpm (1.0 bar-BMEP) to 195°C. An operating mode at the catalyst “wake-up” temperature, defined as Mode 22, 1500 rpm (1.0 bar-BMEP), subsequently replaced the mode 12 point. During the ADVISOR vehicle cycle simulation modeling performed by the National Renewable Energy Laboratory, Mode 22 revealed a high frequency of occurrence for the FTP-75 drive cycle.

The selected operating modes significance to vehicle operation are as follows:

- Mode 22 Catalyst transition temperature
- Mode 11 Low speed cruise
- Mode 10 Low speed cruise with slight acceleration
- Mode 6 Moderate acceleration

#### 5.1.2.1 Rules For Defining Low-NO<sub>x</sub> Operation

Due to the number of test modes and fuels, a set of rules was developed in order to select the operating condition to use for low NO<sub>x</sub> operation. For the modal conditions examined, the rules targeted the five parameters shown in Table 13. A low NO<sub>x</sub> condition was established when EGR was greater than the OEM value, and the combination of EGR and combustion timing was constrained by boost, smoke, fuel consumption, and unburned hydrocarbons.

Table 13. Rules for Defining Low NO <sub>x</sub> Operation							
MODE	Engine Speed	Load, bar-BMEP	EGR	BSFC	BOOST	SMOKE	BSHC
6	2300	4.2	>OEM (16%)	3% maximum increase	50% maximum decrease	100% maximum increase	100% maximum increase
10	2000	2.0	>OEM (33%)	3% maximum increase	50% maximum decrease	100% maximum increase	100% maximum increase
11	1500	2.62	>OEM (35%)	3% maximum increase	>0	100% maximum increase	100% maximum increase
22	1500	1.0	>OEM(51%)	3% maximum increase	NR	100% maximum increase	100% maximum increase

The boost constraint was utilized as a surrogate for drivability, and it was expected to limit the amount of useable EGR. It was decided for modes 10 and 6 that 50% of the OEM boost should be available to maintain reasonable drivability during low NO<sub>x</sub> operation. The 50% target was arbitrary, but was selected to maintain a positive manifold pressure at rational EGR levels. For mode 11, the intake manifold condition was constrained to the normally aspirated case. No boost rule was imposed on the mode 22 condition.

The fuel consumption constraint was a 3% penalty for all modes, compared to the OEM condition with each fuel. The fuel consumption was limited, because the requirements of emission control devices could also add further fuel economy penalty. The fuel consumption penalty was expected to constrain the combustion timing retard.

The smoke and unburned hydrocarbon rules were established to limit soot formation and combustion inefficiency. Smoke and hydrocarbon emissions were allowed to increase, however they should be controlled by diesel oxidation catalysts and diesel particulate traps in vehicles using emission control device technologies. All fuels were tested for each mode under the rules established to determine a new set of operating conditions.

#### **5.1.2.2 Operating Conditions Selection**

The low NO<sub>x</sub> operating conditions, determined in this study for the OM611 engine as a function of EGR and combustion timing, are shown in Table 14. The OEM parameters for each of the four modes selected for the PM characterization study are also included in Table 14. Due to the form of the pressure trace for Mode 6, the crank angle of 50-percent burn (CA<sub>50</sub>, dATDC) gave better resolution for determining the combustion timing. The operating conditions reflect an evaluation of the data sets with respect to the selection criteria previously discussed.

Table 14. OEM and Low NOx Operating Conditions						
Run Mode	OEM			Low NOx		
	EGR, %	LPPm, dATDC	CA50, dATDC	EGR, %	LPPm, dATDC	CA50, dATDC
6	16±1		16±1	25±1		18.5±1
10	33±2	16±1		38±2	19±1	
11	35±2	12.5±1		40±2	16±1	
22	51±1	14±1		56±1	16.5±1	

### 5.1.2.3 Timing Versus EGR Window For All Fuels

Figure 6 shows the new set of EGR rate and combustion timing values, consistent with the predetermined constraints. An operating window of plus and minus two percent for EGR and plus and minus one crankangle degree for timing is shown around the center value. The window was to represent an acceptable control tolerance. But, independently, the EGR and combustion timing for all of the test fuels, which met the low NOx rules, fell within the same tolerance window. This observation indicates that for the fuels evaluated in the OM611 engine, as currently configured, low NOx emissions are constrained by performance parameters, not fuel composition.

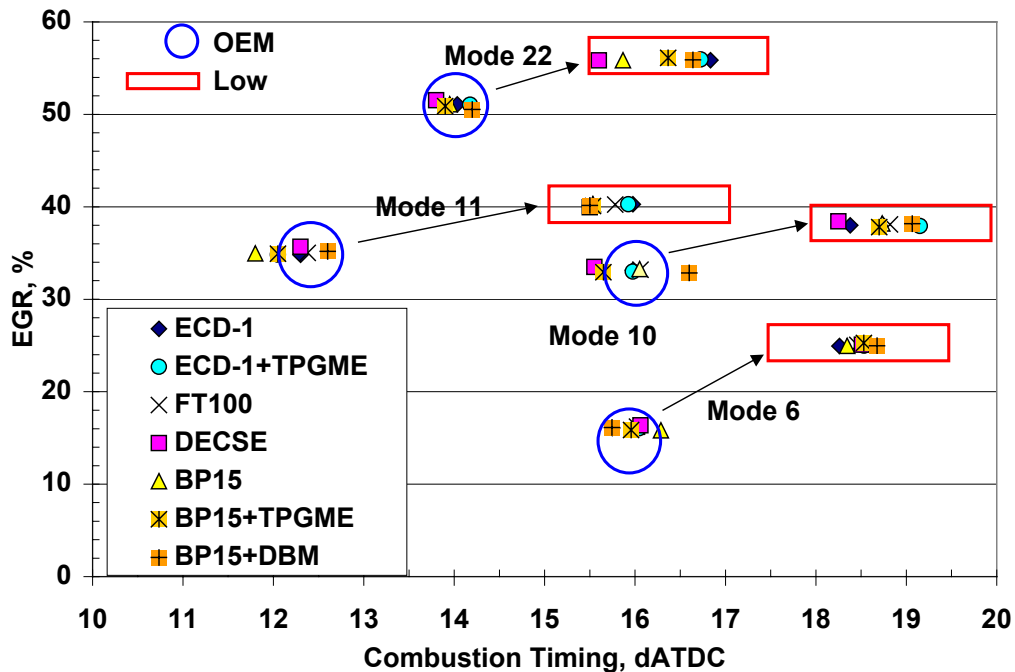


Figure 6. Modal EGR and Combustion Timing Windows for All Fuels

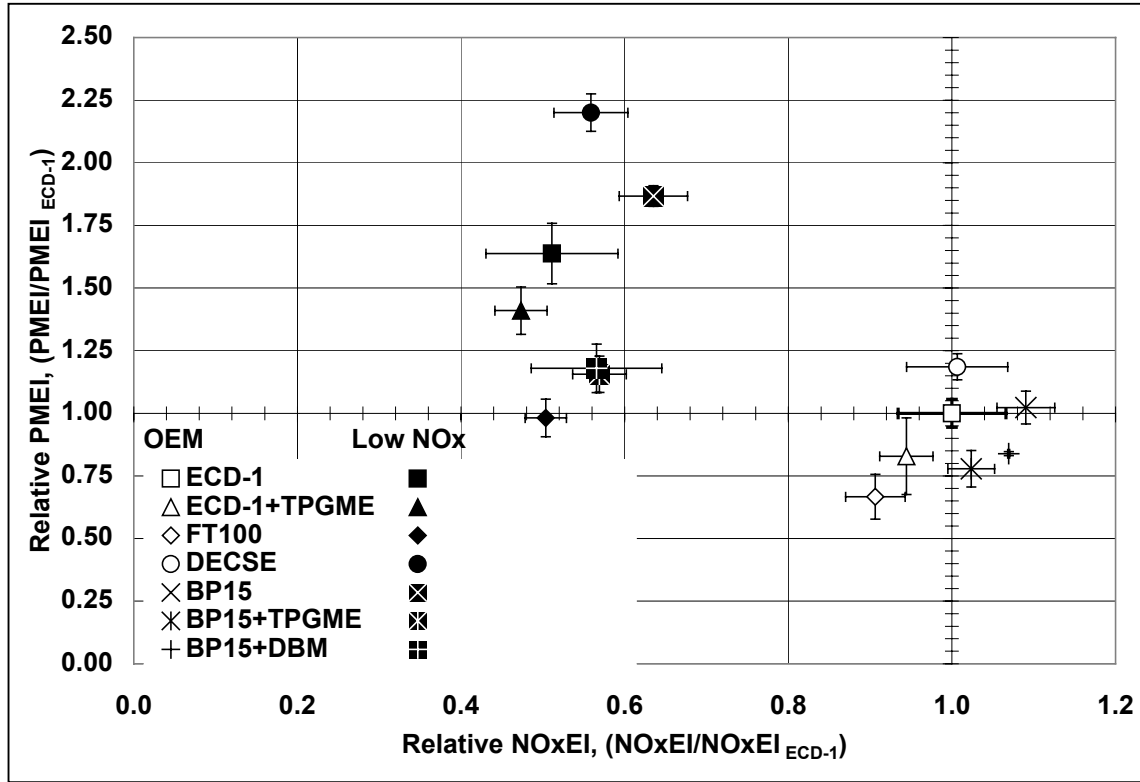
Although the combustion timings were similar for each fuel at the low NOx condition, the physical timings varied to achieve the combustion timing. Table 15 shows the pilot and main start-of-injection timing for each fuel at the OEM and low NOx operating conditions. The low NOx operating condition physical injection timing is not as retarded as the subsequent combustion timing retard seen in Table 14. This is because the increased EGR at the low NOx condition, in acting as a diluent, retards combustion and contributes to the overall timing retard.

<b>Table 15. Injection Timings for Fuels, Modes and Engine Control Condition</b>									
<b>Fuel</b>	<b>Control Condition</b>	<b>Mode 6</b>		<b>Mode 10</b>		<b>Mode 11</b>		<b>Mode 22</b>	
		<b>Pilot SOI*</b>	<b>Main SOI</b>	<b>Pilot SOI</b>	<b>Main SOI</b>	<b>Pilot SOI</b>	<b>Main SOI</b>	<b>Pilot SOI</b>	<b>Main SOI</b>
ECD-1	OEM	29.0	5.0	22.4	1.4	17.8	1.8	15.8	-0.2
	Low NOx	28.4	4.4	21.6	0.6	16.0	0.0	15.9	0.0
ECD-1+TPGME	OEM	28.9	4.9	23.8	2.8	18.8	2.8	16.7	0.8
	Low NOx	28.3	4.3	22.9	1.9	16.7	0.7	17.0	1.1
FT100	OEM	29.3	5.3	20.7	-0.3	17.0	1.0	14.1	-1.8
	Low NOx	28.9	4.9	19.7	-1.3	14.8	-1.2	13.8	-2.2
DECSE	OEM	34.1	7.0	24.0	3.1	18.8	2.8	17.5	1.5
	Low NOx	32.9	5.8	23.1	2.2	17.1	1.1	17.9	2.0
BP15	OEM	30.0	6.0	21.4	0.4	17.2	1.3	15.1	-0.9
	Low NOx	29.8	5.8	20.2	-0.8	15.2	-0.8	14.1	-1.8
BP15+TPGME	OEM	28.0	4.0	22.7	1.7	18.1	2.1	16.1	0.2
	Low NOx	27.0	3.0	21.4	0.4	16.3	0.2	15.9	0.0
BP15+DBM	OEM	29.9	5.9	22.7	1.7	18.5	2.5	17.4	1.4
	Low NOx	28.7	4.7	22.5	1.5	17.0	1.0	18.6	2.7
* SOI = Start of Injection in degrees Before Top Dead Center									

For all of these conditions, EGR rate was increased beyond the OEM value, and the combustion timing was further retarded after top dead center in the expansion stroke. Under these circumstances engine-out NOx emissions are reduced versus OEM conditions. All engine-operating conditions of BSFC, Boost, Smoke and BSHC – regardless of the fuel - fell within the same limits.

Relative weighted emission index values were calculated for the test fuels, with the ECD-1 fuel used as the base. The relative NOx versus PM index trade off is shown in Figure 7. Included in Figure 7 are data for the OEM and low NOx operating condition, with the

results normalized to ECD-1 fuel at the OEM condition. Also included in Figure 7 are estimates of the 95% confidence intervals for the data.



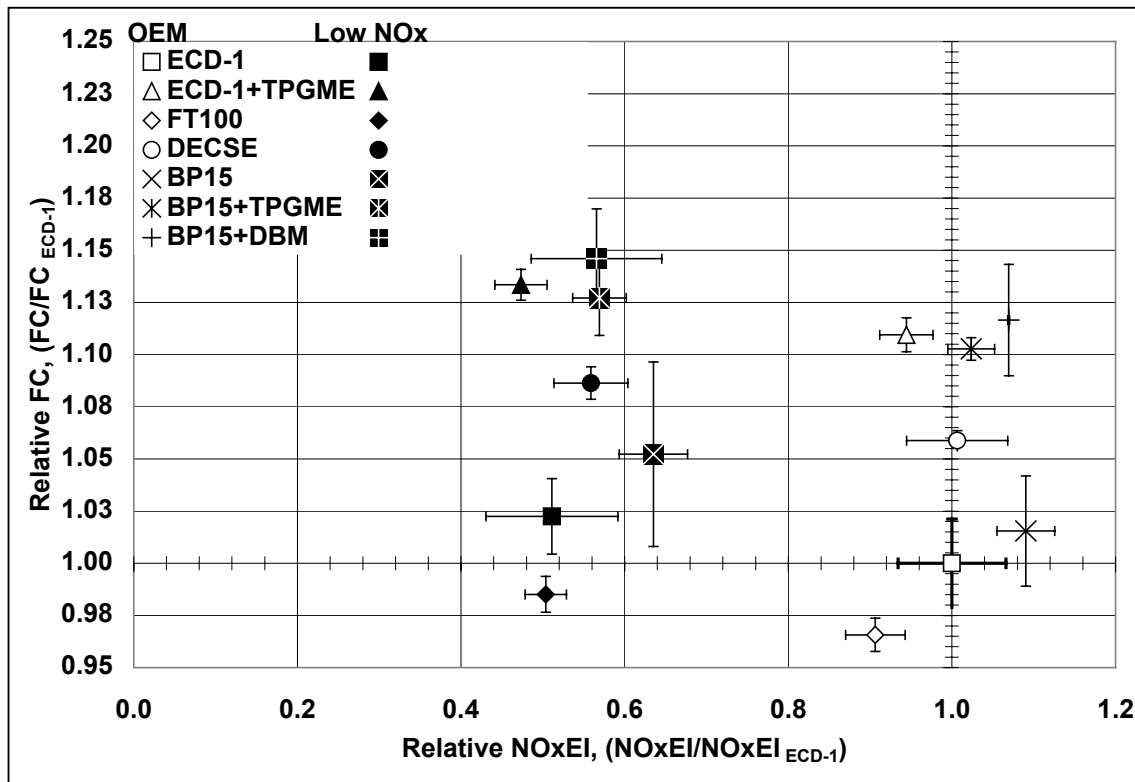
**Figure 7. Weighted Relative NOx versus Relative PM Trade-Off for Test Fuels**

Based on the confidence intervals shown in Figure 7, the OEM condition NOx index of the ECD-1 and DECSE fuels are similar to all other fuels. FT100 is different than the BP15 based fuels, and the BP15 and BP15 based fuels show a greater NOx index than ECD-1+TPGME at the OEM condition. The relative PM index results suggest FT100 and the oxygenated fuels are similar, the ECD-1 and BP15 are similar, and the DECSE fuel is uniquely higher. The BP15 fuel has higher PM response than the BP15-based oxygenated fuels for the OEM condition.

At the low NOx condition all the fuels appear similar in regard to the relative NOx index. The PM index results at the low NOx condition spread apart, with the PM from FT100 being lower than any other fuel. The ECD-1+TPGME is lower than ECD-1, BP15, and the DECSE result. The PM index for the BP15-based oxygenated fuels were unique from

the other fuels at the low NOx condition, yet similar to each other, and only greater than FT100.

Relative weighted fuel consumption was calculated and plotted with respect to relative NOx index in Figure 8 for the OEM and low NOx operating conditions. Overall the fuel consumption penalty for low NOx operation is on the order of 2.5 to 3 percent.



**Figure 8. Weighted Relative NOx versus Relative Fuel Consumption for Test Fuels**

It was possible to decrease mode-weighted NOx emissions compared to the OEM calibration – generally with corresponding increases in other emissions. These emissions increases could be partially overcome with the use of oxygenated fuels. However, increases in fuel consumption and losses in engine boost proved to be more significant in limiting practical NOx control than the emission reduction benefits from fuel composition changes.

Table 16 shows the NOx index reductions for the low NOx operating condition with respect to operating modes, fuels, and their averages. The averages for the fuels across all modes, the modes across all fuels, and the overall arithmetic averages are shown. More details for the determination of the low NOx operating conditions are found in reference 14. The low NOx operating parameters shown in Table 14 were used for the particulate matter characterization testing.

**Table 16. NOx Emission Index Reduction Due to Fuels, Modes, and Averages**

	Mode 6	Mode 10	Mode 11	Mode 22	Fuel Avg. for Modes
ECD-1	53.1%	38.5%	46.1%	55.5%	48.3%
ECD-1 + TPGME	53.8%	39.4%	47.9%	54.9%	49.0%
FT100	49.2%	34.9%	38.3%	47.5%	42.8%
DECSE	48.1%	34.5%	42.2%	48.8%	43.4%
BP15	41.9%	33.3%	44.4%	41.1%	40.2%
BP15 + TPGME	46.1%	37.5%	45.4%	56.9%	46.5%
BP15 + DBM	49.4%	39.9%	46.7%	61.4%	49.3%
Mode Avg. for Fuels	48.8%	36.9%	44.4%	52.3%	<b>45.6%</b>

### **5.1.3 Cylinder Balance**

The DaimlerChrysler OM611 engine will have a Kistler 6052A piezoelectric pressure transducer installed in each of the four cylinders via a glow plug adapter. The cylinder pressures were monitored with a DSP high-speed data acquisition system clocked at 0.5° crankshaft intervals. The DSP data system will be set up to monitor Location of Peak Pressure (LPP), Crank Angle for 50% burn (CA50), and Indicated Mean Effective Pressure (IMEP) for each cylinder. The DSP was also used to calculate engine average IMEP, LPP, and CA50 for 50 consecutive combustion cycles. During testing, the RPECS control system was able to maintain IMEP within 5% cylinder-to-cylinder, and hold LPP or CA50 within 2 crankangle degrees cylinder-to-cylinder for all modes.

The cylinder balance procedure was as follows:

1. Set Test Mode, RPECS will do closed loop torque control by dithering injection duration.
2. Set EGR level.



3. Make individual cylinder timing changes to meet LPP or CA50 value for low NO<sub>x</sub>.
4. Average IMEP for all four cylinders.
5. Adjust individual injection duration offsets to set cylinder IMEP within  $\pm 5\%$  of the average IMEP.
6. Iterate between timing changes and IMEP adjustments.
7. Update Controller tables for timing and duration offsets.
8. Stabilize engine at balanced IMEP and Combustion Timing.
9. Initiate particulate and gaseous emission sampling.
10. Spot Check IMEP and LPP or CA50 during particulate sampling.

#### **5.1.4 Pilot Fuel Injection**

Pilot fuel injection was operational during all testing. The pilot pulsewidth and pilot phasing angle were held constant for each fuel tested. The value of the pilot duration and pilot phasing were dependent on the test mode.

#### **5.1.5 Intake Runner Valve**

The engine has an Intake Runner Valve (IRV) for increasing swirl at low-speeds, light-loads. The IRV works by closing off one of the two intake ports, forcing the entire intake charge down the other intake tract. The status of the IRV under Bosch ECM control is as shown in Table 17 for the test modes considered.

<b>Table 17. Modal Intake Runner Valve Positions</b>			
<b>Mode</b>	<b>RPM</b>	<b>BMEP, bar</b>	<b>IRV Status</b>
22	1500	1.0	Closed
11	1500	2.62	Closed
10	2000	2.0	Closed
6	2300	4.2	Open

For the toxicology study, the IRV was utilized as calibrated by DaimlerChrysler. Changing the in-cylinder charge air motion by varying IRV status could alter combustion and impact the results for the OM611 engine.

## **5.2 Test Plan**

### **5.2.1 PM Analysis II Emission Control System Devices**

The MECA supplier for the emission control devices coated, canned, baked, and delivered the devices to SwRI. The MECA supplier baked the aftertreatment devices in a 600°C oven for 48 hours prior to delivery. The baking was performed to degas the insulation, packing, and washcoat. The baking will reduce the time required to de-green the devices on the engine. A 1.5L diesel oxidation catalyst and a 2.5L catalyzed diesel particulate filter were received. Currently, the test cell exhaust system is being fabricated to include the emission control devices. The exhaust configuration for testing includes a particulate filter diversion branch. The exhaust will be diverted around the DPF when measurements are being taken upstream of the DPF. The exhaust backpressure will be controlled during diversion to simulate the DPF being in the system.

The OM611 engine was operated with both Emission Control Devices (ECD) present, to determine the effect of the ECD on backpressure and engine control. The engine-out backpressure was higher with the ECD installed, however the control of the engine and EGR stability were not affected and the gaseous emissions were within the repeatability of previous tests.

Efforts were extended to develop a regeneration protocol with the DPF. The regeneration target was to obtain 550°C at the DPF inlet, while operating the engine at Mode 6, 2300-rpm/4.2-bar BMEP. The typical exhaust stack temperature for Mode 6 is 395°C. During regeneration, the injection pulse was modified such that the pilot duration was extended to inject ~70% of the fuel with location of the peak pressure of combustion at 7°ATDC. The remaining fuel was injected late cycle, ~45°ATDC. The DOC converts the late cycle injected hydrocarbons into heat for the DPF. The regeneration to a consistent 115 kPa-absolute backpressure from a fully loaded DPF takes 90 minutes to complete. It appears the DOC is consuming >90% of the unburned hydrocarbons and

oxygen, thus resulting in the slow regeneration of the DPF. However, the strategy was to regenerate the DPF at a condition that would not jeopardize the cylinder pressure transducers installed in the engine. Efforts were made to alter the regeneration strategy to shorten the burn-off time. The base soot pack appears to be consistent, as determined by DPF weight, at the 115 kPa-absolute backpressure. Six regeneration cycles to 115 kPa-absolute backpressure revealed a spread of three grams between the maximum and minimum DPF weight recorded.

Efforts were made to develop the base soot pack with the Fischer-Tropsch fuel. After seven load and regeneration cycles the base soot pack appeared to stabilize. The MECA supplier was consulted on the regeneration strategy. The supplier felt the time at temperature would impact the durability of the catalyzed coating on the DPF, and suggested modifying the strategy. The supplier also mentioned they rarely try to get the DPF back to a base backpressure, they burn until the initial high burn rate subsides in order to save fuel.

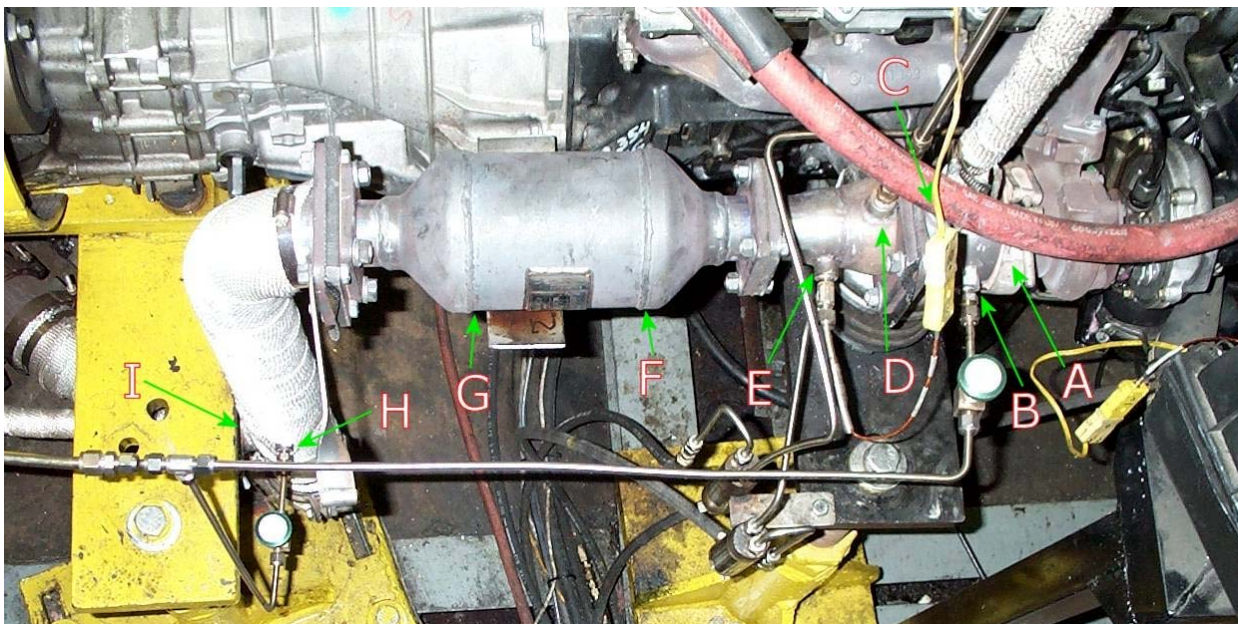
Discussions with the suppliers of the DPFs and the substrate used in the DPFs, and testing by SwRI's Department of Emissions Research (DER), led to an improved strategy for regenerating the filters during testing. After each day's test work, the filters will be removed from the engine system and regenerated by DER on an SI engine. The equipment used for regeneration is better able to simultaneously control temperature and oxygen content, for better control of the burn-off. DER will monitor temperatures and pressure loss to determine when the burn-off is complete. Two identical DPFs will be used alternately to ensure one is always ready for testing. The regeneration strategy will include gradually increasing the exhaust temperature to 600°C over a 15-minute time frame, while maintaining five percent oxygen in the exhaust. When 600°C is attained at the DPF inlet, the conditions will be maintained until the backpressure stops decreasing.

A series of load and regeneration cycles were performed on each of the DPFs to validate regeneration consistency and to stabilize the devices. The regenerated weights and backpressure consistency for both DPFs has been repeatable for three load and burn cycles. Loading times were also varied in order to validate a sampling time for the 90 mm particulate sampling filters

downstream of the DPFs. SOF will not be measured downstream of the DPFs; so sample time will be determined by the need to keep the DPF loadings below 17g.

Table 18 in conjunction with Figures 9 and 10 show the changes to the exhaust system for the DC OM611 engine to incorporate the three sampling locations. The oxidation catalyst (F,G: Figure 9) had to be moved slightly downstream from a close-coupled position to accommodate the sampling and instrumentation probes. The catalyzed DPF (N, O, Figure 10) is located at the position downstream which would correspond to an under floor location on a vehicle.

<b>Table 18. OM611 Instrument and Sample Port Location Key for Figures 9 and 10</b>		
<b>Reference</b>	<b>Distance downstream of TC Outlet Flange [mm]*</b>	<b>Instrument / Port</b>
A	0	Turbocharger Outlet Flange
B	30	Gaseous Emissions sampling port (engine-out)
C	60	Particulate Emissions Sampling Port (engine-out)
D	110	CO2 Sampling port
E	145	Temperature, Pressure (Engine-out)
F	280	Front face of Catalyst material
G	420	Rear Face of Catalyst Material
H	985	Gaseous Emissions Sampling port (Catalyst-out)
I	1055	Particulate Emissions Sampling Port (Catalyst-out)
J	1335	Pressure (Catalyst-out)
K	1460	Y Fitting in Pipe
L	1490	Temperature (Catalyst-out)
M	1685	Butterfly valve to isolate DPF
N	1990	Front Face of DPF Material
O	2115	Rear Face of DPF Material
P	2330	Thermocouple
Q	2485	Y Fitting in Pipe
R	2535	Temperature, Pressure (DPF-out)
	4440	Gaseous Emissions Sampling port (DPF-out)
	4770	Smoke probe
	4945	Particulate Emissions Sampling Port (DPF-out)
* Distances are approximate, rounded to nearest 5 mm		



**Figure 9. OM611 Engine-Out and Catalyst-Out Instrumentation and Sampling Configurations**



**Figure 10. OM611 Catalyzed Diesel Particulate Filter Instrumentation and Sampling Configuration**

### **5.2.2 PM Characterization Test Fuels**

The Ad-Hoc Steering Committee, which includes DOE, designated the test fuel matrix as a subset of the matrix of fuels that were evaluated in the low NO<sub>x</sub> operation program. The dimethoxymethane used to add oxygen to the fuel in the previous study was replaced by two oxygen containing compounds identified in a DOE/Auto-Energy fuel oxygenate study. The finalized four-fuel matrix included the following:

<b>Fuel Number</b>	<b>Description</b>
1	BP15, a 15 ppm sulfur diesel fuel prepared by processing straight-run distillate stocks through a commercial, single-stage hydrotreater employing a high-activity catalyst at maximum severity. This fuel was prepared in a commercial refinery unit (not a pilot plant), but cracked stocks were excluded from the feed because the specification sulfur level could not have been achieved with their inclusion. Year 2007 actual production will likely employ more advanced processing to allow the inclusion of cracked stocks.
2	A fuel blend of the BP15 low sulfur fuel with tripropylene glycol monomethyl ether added to achieve seven weight percent oxygen.
3	A fuel blend of the BP-15 low sulfur fuel with dibutyl maleate added to achieve seven weight percent oxygen.
4	FT100, Neat Fischer-Tropsch fuel.

### **5.2.3 PM Characterization Test Modes**

Three engine operation modes were eventually tested: Modes 6, 11, and 22. The specific engine operating parameters, such as injection timing for location of peak pressure, and percentage EGR were approved by the Ad-Hoc Steering Group, and carried forward from the low NO<sub>x</sub> operation program phase. The goal is to use specific engine operating

parameters that may be used to meet future NO<sub>x</sub> and PM emissions standards. The engine calibration settings determined by SwRI<sup>®</sup> are shown in Table 19. Each engine operating mode, fuel, and location of emission sampling will be done in triplicate.

<b>Table 19. Modal Operating Conditions Reflecting Low Engine Out NO<sub>x</sub> Operation.</b>							
Run Mode	BMEP, bar	Engine Speed, rpm	OM611 Equiv. Torque, ft-lbf	EGR, %	LPPm, dATDC	CA50, dATDC	Exhaust Temp., °C
22	1.0	1500	12.6	56±1	16.5±1		195
11	2.62	1500	33.1	40±2	16±1		290
6	4.20	2300	53.0	25±1		18-19	350

The complete set of toxicologically relevant compounds (benzene, 1,3-butadiene, formaldehyde, acetaldehyde, gas phase PAH, particle phase PAH, soluble organic fraction, and particulate matter) were measured before the close-coupled oxidation catalyst (engine out), and after the oxidation catalyst. Only gas-phase PAH, PM mass, benzene, 1,3-butadiene, formaldehyde, and acetaldehyde were measured after the particle trap. It was the responsibility of the analytical chemist to determine the appropriate GC-MS method for PAH analyses. A "non-detect" was only accepted if the concentration of the PAH was below the detection of the most sensitive method available (HRGC-MS).

#### **5.2.4 PM Characterization Test Procedures**

Testing will tentatively be performed as follows:

1. Assemble engine exhaust aftertreatment system; provide appropriate backpressure instrumentation. Develop DPF bypass exhaust system, with backpressure control system
2. De-green emission control devices
  - Utilize ~2ppm S fuel
  - Utilize specified procedures
3. Establish DPF Regeneration Scheme with ~2ppm S fuel
  - Establish base soot pack
  - Validate regeneration consistency to base backpressure



- Establish DPF weight to backpressure relationship for regeneration
  - Establish modal backpressure and filter differential pressure control target
  - Eventually, off-line regeneration was chosen
4. Establish testing protocols with BP-15 fuel
  5. Generate system and tunnel blanks for 90mm and PUF/XAD-2 filters
  6. Initiate fuels testing with BP-15 test fuel
    - Flush and drain fuel system. Flush and fill fuel system with test fuel and new filter
    - Drain engine oil and discard oil filter. Fill engine with new oil and new filter
    - Operate engine to age engine oil and load DPF and regenerate with BP-15 fuel to establish fuel specific soot pack
    - Initiate test day
      - Install clean DPF
      - Warm up engine on Mode 11 low NOx condition, checking engine out gaseous emissions and smoke
      - Perform steady-state evaluations at selected test mode
      - DPF Out, monitoring DPF back pressure
        - 30-minute tunnel stabilization
        - Sampling interval TBD, mode dependent
      - Oxidation Catalyst Out, monitoring engine back pressure
        - 30-minute tunnel stabilization
        - Sampling interval TBD, mode dependent
        - Bypass DPF, control engine back pressure
      - Engine Out, monitoring engine back pressure
        - 30-minute tunnel stabilization
        - Sampling interval TBD, mode dependent
        - Bypass DPF, control engine back pressure
    - Remove and regenerate DPF
      - Repeat test day, items a) through g), until four modes and three repeats have been completed for BP-15 fuel.



7. Perform Step 6 with BP-15 + tripropylene glycol monomethyl ether added to achieve 7-weight percent oxygen.
8. Generate system and tunnel blanks for 90mm and PUF/XAD-2 filters.
9. Perform Step 6 with BP-15 + dibutyl maleate added to achieve 7-weight percent oxygen.
10. Perform Step 6 with FT100 fuel.
11. Generate final system and tunnel blanks for 90mm and PUF/XAD-2 filters.

## **6.0 FUEL IMPACT ON EMISSIONS – MODE EFFECTS**

Fuel comparisons were made for the modal brake specific exhaust emissions with the engine operated under EGR and combustion timing control with the pilot fuel injection. The results for Mode 6 can be found in Appendix B, Mode 11 in Appendix C, and Mode 22 in Appendix D. Each of appendices B-D have data plotted representing the 95% confidence intervals for triplicate runs, are in the same plot order, and show each sample location. The first seven plots represent engine control parameters and engine response data. The data suggests for each mode, with all fuels, and at each sample location that the combustion timing and EGR targets were achieved within the allowable tolerances.

### **6.1 Fuel Impact on Regulated Brake Specific Mass Emissions – TFLRF/SwRI Observations**

#### **6.1.1 Fuel Impact on CO**

Data for Mode 6 (Figure B-8) suggest there is no difference in CO emissions between BP-15 and BP-15 plus TPGME fuels at the engine-out sample. BP-15 plus DBM emits more CO than any other test fuel. FT100 had the lowest CO emissions at Mode 6 engine-out. CO was fully converted at the catalyst-out and DPF-out sample locations for all test fuels at Mode 6.

Data for Mode 11 (Figure C-8) suggests there are differences between all the BP-15 containing fuels. The rank from least to greatest Mode 11 engine-out emissions is

FT100, BP-15, BP-15 plus TPGME, and then BP-15 plus DBM. The CO was fully converted at the catalyst out and DPF-out sample locations for all test fuels at Mode 11.

Data for Mode 22 (Figure D-8) engine-out suggests there are differences between BP-15 and the BP-15 oxygenated fuels. The two oxygenated fuels show similar results. The rank from least to greatest Mode 11 engine-out emissions is FT100, BP-15, BP-15 plus TPGME, and then BP-15 plus DBM. The CO was reduced, but not fully converted at the catalyst out and DPF-out sample locations for all test fuels at Mode 22. The fuel order results after the emission control devices reflects the order at engine-out.

### **6.1.2 Fuel Impact on HC**

Data for Mode 6 (Figure B-9) suggests there is little difference in HC emissions between BP-15, BP-15 plus TPGME, and BP-15 plus DBM fuels at the engine-out sample. FT100 had the lowest HC emissions at Mode 6 engine-out. The HC were reduced significantly at the catalyst out and DPF-out sample locations for all test fuels at Mode 6, such that little difference was seen between fuels with respect to HC emissions.

Data for Mode 11 (Figure C-9) suggests there are differences between all the BP-15 containing fuels. The rank from least to greatest Mode 11 engine-out HC emissions is FT100, BP-15 plus DBM, BP-15 plus TPGME, and then BP-15. The HC was greatly reduced at the catalyst out and DPF-out sample locations for all test fuels at Mode 11. There are only small differences in HC emissions after the emission control devices.

Data for Mode 22 (Figure D-9) engine-out suggests there are large differences between BP-15 and the BP-15 oxygenated fuels. The two oxygenated fuels show similar results. The rank from least to greatest Mode 11 engine-out emissions is FT100, BP-15, BP-15 plus TPGME, and then BP-15 plus DBM. The HC were only slightly reduced, at the catalyst out and DPF-out sample locations for all test fuels at Mode 22. The BP-15 plus TPGME fuel showed an increase of HC emissions after the ECD, but there is variation of the test data.

### **6.1.3 Fuel Impact on NO<sub>x</sub>**

Data for Mode 6 suggests there is very little variation in NO<sub>x</sub> emissions between any fuel and any sample location. FT100 appeared to have the highest NO<sub>x</sub> at all sample locations. The emission control devices are not doing any NO<sub>x</sub> conversion.

Data for Mode 11 suggest differences between all the BP-15 containing fuels for engine-out NO<sub>x</sub> emissions. The BP-15 and FT100 fuels show similar NO<sub>x</sub> response. The BP-15 plus TPGME fuel had the lowest NO<sub>x</sub> response. The emission-control devices do not appear to be doing any NO<sub>x</sub> conversion, and post-device results are similar to engine-out results.

Data for Mode 22 engine-out suggests there are differences between BP-15 and the BP-15 oxygenated fuels. The two oxygenated fuels show similar results. The rank from least to greatest Mode 11 engine-out NO<sub>x</sub> emissions is BP-15 plus DBM, BP-15 plus TPGME, BP-15, and then FT100. Discounting measurement variations, the emission control devices do not appear to be doing any NO<sub>x</sub> conversion, and post device results are similar to engine-out results

### **6.1.4 Fuel Impact on PM**

At Mode 6 the data suggests that engine-out PM emissions for the oxygenated fuels and FT100 are similar, and less than the BP-15 fuel. Except for the BP-15 plus DBM fuel, there were PM reductions after the oxidation catalyst. Results after the DPF showed no difference between the test fuels.

The Mode 11 data suggests that engine-out PM emissions for BP-15 plus TPGME and FT100 are similar, and less than the BP-15 fuel. The BP-15 plus DBM fuel revealed the greatest PM emissions engine-out. There were PM reductions after the oxidation catalyst for all test fuels. Results after the DPF showed no difference between the test fuels for Mode 11.

For Mode 22 the data suggests that engine-out PM emissions for BP-15 plus TPGME and BP-15 plus DBM are greater than both FT100 and the BP-15 fuel. The BP-15 plus DBM fuel revealed the greatest Mode 22 PM emissions engine-out, FT100 the least. There were PM reductions after the oxidation catalyst for all test fuels. Results after the DPF revealed small differences between the BP-15 and FT100 test fuels, and higher PM results for the oxygenate blends.

#### **6.1.5 Fuel Impact on SOF of PM**

The engine-out SOF at Mode 6 is similar for all test fuels. Except for the BP-15 plus TPGME fuel, there were SOF increases after the oxidation catalyst, although there was significant variation in some of the results. It had been anticipated that the oxidation catalyst would destroy SOF.

The Mode 11 data suggests that engine-out SOF emissions for BP-15 plus TPGME and BP-15 are similar and greater than the BP-15 plus DBM and FT100 fuels that are similar. There was SOF reductions after the oxidation catalyst for all test fuels for Mode 11.

Like Mode 11, the Mode 22 data suggests that engine-out SOF emissions for BP-15 plus TPGME and BP-15 are similar and greater than the BP-15 plus DBM and FT100 fuels that are similar. SOF reductions after the oxidation catalyst were seen for all test fuels for Mode 22.

### **6.2 Fuel Impact on Four Clean Air Act Toxic Air Pollutants**

The following discussions summarize the data for CAA toxic-compounds emission response, which can be found in Appendices B, C, and D (Figures 13-16) for the modal operation.

#### **6.2.1 1,3-Butadiene**

The least to most emission fuel rank for 1,3-Butadiene at Mode 6 engine-out is BP-15

plus TPGME, FT100, and BP-15, then BP-15 plus DBM. The emission control devices destroy most of the 1,3-Butadiene at Mode 6.

The best to worst fuel rank for 1,3-Butadiene at Mode 11 engine-out is FT100, BP-15 plus DBM, BP-15 plus TPGME, and then BP-15. The emission control devices destroy most of the 1,3-Butadiene at Mode 11.

The least to worst fuel rank for 1,3-Butadiene at Mode 6 engine-out is FT100, BP-15, BP-15 plus TPGME, and then BP-15 plus DBM. The emission control devices do not destroy the 1,3-Butadiene at Mode 22. In fact for most fuels, 1,3-Butadiene increases after both the oxidation catalyst and the catalyzed DPF during Mode 22 operation.

### **6.2.2 Benzene**

The least to most emission fuel rank for Benzene at Mode 6 engine-out is FT100, BP-15 plus DBM, BP-15 plus TPGME, and then BP-15. The emission control devices destroy most of the Benzene at Mode 6. Results for BP-15 show significantly more Benzene after the ECD than any of the other fuels at Mode 6.

The Mode 11 Benzene emissions reveal the same trends as the 1,3-Butadiene emissions at all locations.

The engine-out Benzene emissions exhibited the same trends as the Mode 22 1,3-Butadiene emissions. The emission control devices do not destroy the Benzene for Mode 22. In fact for most fuels, Benzene increases after both the oxidation catalyst and the catalyzed DPF during Mode 22 operation.

### **6.2.3 Aldehydes**

The Formaldehyde and Acetaldehyde emissions are discussed jointly because they tend to trend the same way. For Mode 6 engine-out the aldehyde emissions rank from BP-15 as lowest, FT100, BP-15 plus DBM, through BP-15 plus TPGME. The aldehydes

are reduced substantially by the oxidation catalyst, but increase slightly after the catalyzed DPF. The Mode 11 Aldehydes reveal the same trends as the Mode 6 data.

For the Mode 22 engine-out the aldehyde emissions rank from FT100 as lowest, BP-15, BP-15 plus TPGME, through BP-15 plus DBM. The aldehydes for the oxygenated fuels are significantly greater than the other fuels. At Mode 22 the aldehydes are reduced substantially by the oxidation catalyst, but increase slightly after the catalyzed DPF. The Mode 11 aldehydes reveal the same trends as the Mode 6 data.

#### **6.2.4 Acetaldehyde**

Statistically significant differences were apparent in the average acetaldehyde among the fuels, modes, and fuel mode interaction. Average acetaldehyde for the FT-100 and ADMM15 fuels are not significantly different from one another. The average acetaldehyde for the ALS, CA, and DF-2 fuels are not significantly different from one another, but are significantly different from the FT-100 and ADMM15 fuels.

There are three distinct mode groupings with respect to the average acetaldehyde. Modes 10 and 11 are significantly different from one another and the remaining two modes. Modes 5 and 6 are not significantly different from one another but are significantly different from the other two modes.

The ALS and DF-2 fuels have significantly different average acetaldehyde at modes 10 and 11 than at the remaining two modes. All other fuels do not demonstrate this difference. However, the average acetaldehyde for the CA fuel at mode 10 is significantly different than the other three modes.

### **6.3 Fuel Impact on Gaseous PAH Species**

Due to the substantial amount of data, the gaseous phase PAH species emission response will be discussed in terms of general trends. The species will be discussed as groupings by molecular weight. The discussions to follow are summaries of the data for gaseous

phase PAH compounds emission response which can be found in appendices (B, C, D: Figures 17-28) for the modal operations.

### **6.3.1 Pyrene, Fluoranthene, Anthracene, Phenanthrene**

The general trends for these higher molecular weight gas-phase PAH compounds is that the oxygenated fuels are equivalent to FT100 fuel at Mode 6 engine-out operation and lower than BP-15. Furthermore the trend is for the compound emissions to remain constant or increase as they pass through the emission control devices.

The trends for these higher molecular weight gas-phase PAH compounds at Mode 11 is that the oxygenated fuels are equivalent or slightly greater than the FT100 fuel for engine-out operation and greatly lower than BP-15. The trend is for these compound emissions to remain constant or decrease as they pass through the emission control devices at Mode 11.

The Mode 22 results for Pyrene and Fluoranthene follow the same trends as the Mode 11 data for the test fuels. The oxygenated fuels show a large response for Anthracene and Phenanthrene for Mode 22. The emission control devices reduce the Anthracene and Phenanthrene emissions for Mode 22, all fuels.

### **6.3.2 Fluorene, Acenaphthene, Acenaphthylene, 2,6-Dimethylnaphthalene**

These compounds at Mode 6 reveal the oxygenated fuels to be greater emitters than FT100, but less than BP-15 for engine-out emissions. The oxidation catalysts destroy these compounds to the extent that except for the BP-15 fuel, the test fuel responses are the same. The catalyzed DPF does not appear to destroy these compounds further at Mode 6.

Except for the greater magnitude of the emission results, the same general trends hold for the Mode 11 data as the Mode 6 data. There is anywhere from five times to an order of magnitude greater mass emission rate for Mode 11 for these compounds.

The Mode 22 mass emission rates are about three orders of magnitude greater than at Mode 6. The oxygenated fuels have greater emissions of these compounds than FT100 (the lowest) and BP-15 fuels. The emission control devices do reduce the levels of these compounds at Mode 22, but not substantially. There are still significant differences between fuels after the devices.

### **6.3.3 Biphenyl, 1-Methylnaphthalene, 2-Methylnaphthalene, Naphthalene**

The general trends for these lower molecular weight gas-phase PAH compounds is that the oxygenated fuels are greater emitters than FT100 fuel at Mode 6 engine-out operation, but lower than BP-15. The compound emissions are mitigated as they pass through the emission control devices, such that all fuels appear equivalent at the tailpipe for Mode 6.

The trends for these lower molecular weight gas-phase PAH compounds at Mode 11 is that the oxygenated fuels are greater than the FT100 fuel for engine-out operation and slightly lower, to equivalent emitters than BP-15. The trends for these compound emissions are to remain decrease as they pass through the emission control devices at Mode 11. All fuels appear equivalent after the emission control devices.

The oxygenated fuels have much greater emissions of these compounds than FT100 (the lowest) and BP-15 fuels. The emission control devices do reduce the levels of these compounds at Mode 22, but not substantially. There are still significant differences between fuels after the devices. The BP-15 plus TPGME fuel reveals some increase in these compounds after the emission control devices for Mode 22.

## **6.4 Fuel Impact on Particulate Soluble Extract PAH Species**

The particulate soluble extract PAH was evaluated at the engine-out sample location and at the catalyst-out locations. Due to the substantial amount of data, the soluble extract PAH species emission response will be discussed in terms of general trends. The species



will be discussed as groupings by molecular weight. The discussions to follow are summaries of the data for particulate soluble extract PAH compounds emission response which can be found in appendices (B, C, D: Figures 29-45) for the modal operations.

#### **6.4.1 Benzo[ghi]perylene, Dibenzo[a,h]anthracene, Indeno(1,2,3-cd)pyrene**

These high molecular weight PAH compounds exhibit similar response for the BP-15 containing fuels which differs from FT100 Mode 6 engine-out. Some of the oxygenated fuel results at engine-out are equivalent to FT100, but the post catalyst results show an increase in emissions for BP-15 containing fuels.

The Mode 11 engine-out and catalyst-out show similar trends for the fuels as Mode 6. The catalyst-out emissions increases are reduced compared to the Mode 6 data.

The Mode 22 data shows substantial increases for these compounds at engine-out for the oxygenated fuels compared to FT100 and BP-15. However, the catalyst-out emissions appear equivalent for all test fuels at Mode 22.

#### **6.4.2 Benzo[a]pyrene, Benzo[e]pyrene, Benzo[k]fluoranthene**

The Benzo[a]pyrene emissions at Mode 6 appear equivalent for all test fuels and sample locations when data variations are considered. The data at Mode 6 suggest Benzo[a]pyrene is not substantially reduced by the oxidation catalyst. The other PAH compounds reveal the oxygenated fuels to be similar to FT100, both engine-out and post-catalyst at Mode 6.

The Mode 6 observations for the soluble PAH compounds are also seen for the Mode 11 engine-out and catalyst-out data.

The Mode 22 data shows substantial increases for these compounds at engine-out for the oxygenated fuels compared to FT100 and BP-15. However, the catalyst-out emissions appear equivalent for all test fuels at Mode 22 for these compounds.

#### **6.4.3 Benzo[b]fluoranthene, Chrysene, Benzo[a]anthracene, Pyrene**

Except for the PAH Benzo[a]anthracene, the other compounds reveal the oxygenated fuels to respond similar to FT100, with lower emissions than BP-15 at Mode 6 engine-out. The post-catalyst data suggest the fuels are equivalent at Mode 6. The Mode 6 Benzo[a]anthracene results reveals all BP-15 fuels to be similar at engine-out and catalyst-out, with the FT100 response substantially lower.

The Mode 11 data shows the oxygenated fuels having a lower emission response than BP-15, but slightly greater than FT100 at engine-out and catalyst-out. The post-catalyst data shows all fuels to be similar for these PAH emissions when data variations are factored.

At Mode 22 the soluble PAH emissions for engine-out are higher for the oxygenated fuel blends. Benzo[b]fluoranthene emission results appear to be the same for all fuels after the oxidation catalyst. The results for the other PAH compounds track the results seen for engine-out, the oxygenated fuels are higher emitters post-catalyst than the other fuels.

#### **6.4.4 Fluoranthene, Anthracene, Phenanthrene, Fluorene**

For Mode 6 engine-out and post-catalyst the emissions results for the oxygenated fuels track with the FT100 fuel, and are substantially reduced from BP-15. BP-15 has unique catalyst-out emission levels; all other fuels appear equivalent for these compounds.

The Mode 11 results align with the results seen for Mode 6 for these PAH compounds both engine-out and catalyst-out.

The trend seen for virtually every other extract PAH compound, both engine-out and post-catalyst for Mode 22, continues for these compounds. The oxygenated fuels have higher emissions of these compounds during Mode 22 operation.

#### **6.4.5 Acenaphthene, Acenaphthylene, Naphthalene**

During Mode 6 operation the emission response for Acenaphthene and Naphthalene show

similar trends: the engine-out results for all fuels appear equivalent and the emissions of these compounds increase after the oxidation catalyst. The Acenaphthylene findings reveal the oxygenated fuels are equivalent to FT100, both engine-out and catalyst-out, and lower than BP-15.

A trend similar to that seen in the Mode 6 data is also seen in the Mode 11 results, except for larger variations in the data.

The Mode 22 data shows the oxygenated fuels to have higher emissions for these compounds than FT100 or BP-15 at engine-out. The Acenaphthylene data indicate the oxygenated fuels are equivalent to the other fuels post-catalyst at Mode 22. The Naphthalene emissions at Mode 22 do not increase post-catalyst.

## **6.5 Mode Impact On Emissions - Fuel Effects**

The results for BP-15 can be found in Appendix E, BP-15 plus DBM in Appendix F, BP-15 plus TPGME in Appendix G, and FT100 in Appendix H. Each of appendices E-H have data plotted representing the 95% confidence intervals for triplicate runs, are in the same plot order, and show each sample location. The first seven plots represent engine control parameters and engine response data. Appendix E, F, G, and H show plots of the data previously discussed, but sorted to reveal the magnitude of variation between Mode emission levels for each of the test fuels.

## **6.6 Statistical Analysis**

A statistical analysis using a General Linear Model (GLM) of engine, exhaust species, and fuels data for Mode 6 and Mode 11 can be found in reference 31. A GLM procedure was also used to analyze the emissions data for Mode 22 with Fischer-Tropsch fuel as discussed in reference 32. The procedure uses least squares for the dependent variable by one or more factors. The mass emission rate (mass per kilowatt-hour e.g. g/kWh or  $\mu$ g/kWh) was the dependent variable. Except for fuel consumption and NO<sub>x</sub>, all

dependent variables were transformed to their natural logarithm before statistical analysis.

In reference 31, for two emission sets, gas-phase PAH and particle-bound PAH, a factor composed of all of the PAHs from that category (Compound) was used in the ANOVA. For example, the ANOVA for gas-phase PAHs included a factor (Compound) composed of the 12 PAH shown in Table 6; the ANOVA for particle-bound PAHs had a factor composed of the 17 PAHs shown in Table 7. The Scheffé multiple comparisons test was used in a post hoc analysis to determine which means were significantly different. The significance level of the Scheffé test is designed to allow all possible linear combinations of group means to be tested, not just pair wise comparisons.

In reference 32, the possible independent variables were sampling location (Position), engine operating modes (Run Mode), their cross product (Mode x Position), and variables related to oxidation catalyst (OX CAT) and DPF (DPF) operation for Mode 22 2 [31]. The analysis was designed to estimate least square means for emissions so that aftertreatment device efficiency could be calculated. Initially all the dependent variables were regressed against all the independent variables. These results were used to determine outliers that had large studentized residual values ( $>2.5$ ).

It was apparent that repeat runs for Mode 22 were affected by some uncontrolled factor. Engine-out emissions were consistent except for one low point each for formaldehyde and acetaldehyde. Catalyst-out emissions were low for the first two runs, but high for the last run. DPF-out emissions were high for the first and third runs, but low for the second run. The higher molecular weight emissions do not show significant variation over the triplicates. These results indicate that the engine was operating consistently over the runs, but that the aftertreatment devices were changing. Relevant data show that temperature was reasonably consistent during the sampling period of each location so there are no obvious reasons to suspect differences due to temperature. Because the data were taken from five different analyses (viz. FID, IR, GC, HPLC, GC/MS) it is very unlikely that the results are caused by analytical instrument shifts. A possible explanation is that the

oxidation catalyst was inactive during some of the sampling periods. To categorize the data, two nominal variables, OX CAT and DPF, with values “low” or “high” were created to correspond to emission levels. Previous results [32] showed that the DPF had no effect on these gaseous emissions during Modes 6 and 11 operations. Because Mode 22 aftertreatment system temperatures were lower than Modes 6 and 11, it is likely that the oxidation catalyst activity alone explains the variation.

## **7.0 CONCLUSIONS**

The project plan was fully coordinated with DOE and Industry through the Auto/Energy CIDI Ad Hoc Fuels Group. The industrial leaders specified the cylinder balance approach, specified the targets and speed/load points for low NO<sub>x</sub> engine emission operation. The engine operating parameters of combustion timing and EGR for meeting the low NO<sub>x</sub> targets were determined. The engine installation was modified to adapt a diesel oxidation catalyst and a catalyzed diesel particulate filter. All fuels were evaluated in triplicate for three modes, three sample locations, with pilot fuel injection, IMEP of cylinders balanced within 5%, and the combustion timing and EGR controlled for low NO<sub>x</sub> operation.

The Auto/Energy CIDI Ad Hoc Fuels Group performed detailed analyses and extensive review of the engine and emissions data, Reference 31 and 32. Detailed analyses based on the Auto/Energy CIDI Ad Hoc Fuels Group findings are presented later in this document. The following general conclusions are based on observations of trends in the data:

For the emissions of CO and HC, the emission control devices make the fuels appear equivalent. There was very little variation in NO<sub>x</sub> emissions between the fuels, and there was not any conversion of NO<sub>x</sub> by the emission control devices. The oxygenated diesel fuels reduce PM emissions but not to the level FT100 fuel does. The emission control devices, specifically the diesel particulate filter, make all the fuels appear equivalent with respect to tailpipe PM emissions.

For low NO<sub>x</sub> engine operation at Modes 6 and 11, oxygenated diesel fuel does not lower the emissions of acetaldehyde or formaldehyde, 1,3-butadiene or benzene compared to the BP-15 or FT100 fuels at engine out. The emission control devices effectively make all fuels appear equivalent for these compounds.

For low NO<sub>x</sub> engine operation at Modes 6 and 11, oxygenated diesel fuel lowers Gas Phase PAH emissions compared to BP-15, and is similar to the FT100 fuel. The emission control devices convert most of the gas phase PAH compounds, and all fuels appear equivalent.

For low NO<sub>x</sub> engine operation at Modes 6 and 11, the solid phase PAH emissions appear problematical, in that there appears to be molecular weight effect on the “formation” of certain PAH during the Oxidation Catalyst stage. Exceptions aside, the oxidation catalyst does reduce solid phase PAH levels, with less variations between the fuels.

The Mode 22 data revealed variations not expected with the test fuels at the low NO<sub>x</sub> operating conditions. It has been suggested the low NO<sub>x</sub> operating condition at Mode 22 may have been too aggressive in terms of EGR. Another issue is the pilot fuel injection quantity at Mode 22 may be more critical than the other modes. Due to the lower energy content of the oxygenated fuels, the constant pilot duration may have compromised ignition with the oxygenated fuels at Mode 22.

Previously it was shown that one could take advantage of the low PM emitting properties of oxygenated diesel fuel additives to lower-engine out NO<sub>x</sub> (14). In this study the approach was to see if using this altered engine strategy, which involved the beneficial use of oxygenated Diesel fuel additives, would emit more compounds of toxicological concern than using the base fuel alone. The complete analysis of engine data and exhaust species data can be found in reference 31, but the general results for operating Mode 6 and Mode 11 include:

- The results suggest that these oxygenated Diesel fuel additives can be used to lower engine out NO<sub>x</sub> emissions without risking any increases in tailpipe emissions of compounds of toxicological concern.
- The emissions of toxicologically relevant compounds using the two oxygenated fuels were equivalent to or less than emissions from the FT100 fuel, a recognized clean fuel.
- Two notable exceptions were for particle and gas-phase PAHs where the emissions of compounds for the two oxygenated fuels were higher than the FT100 fuel. The low levels of PAHs from the Fisher-Tropsch fuel may reflect the absence of aromatic compounds present in unburned fuel.

Detailed statistical analysis from reference 32 suggest the following results for low-speed, low-load idle type operation, Mode 22, with aftertreatment devices and Fischer-Tropsch fuel:

- Mode 22 operation significantly increased all measured engine-out brake specific gaseous carbon-containing emissions compared to Modes 6 and 11. This result was expected because of its low operating temperature. The generally low engine-out data variability for these species indicated that this operating condition could be reproduced satisfactorily.
- Catalyst-out and DPF-out data variability for these species indicated that aftertreatment device performance jumped between two states, one giving high emissions and one giving low emissions. In the “low” emission state, the oxidation catalyst’s efficiency during Mode 22 operation was comparable to Modes 6 and 11 operations. In the “high” Emissions State, the oxidation catalyst displayed significantly reduced efficiency (CO, gaseous naphthalene, gaseous 1-methyl naphthalene, gaseous 2-methyl naphthalene, and gaseous biphenyl) or had no

statistically significant effect (hydrocarbon, formaldehyde, acetaldehyde, 1,3-butadiene, and benzene).

- For higher molecular weight gaseous PAH's, there was no statistically significant difference between the "high" and "low" emission states of the oxidation catalyst or DPF. During Mode 22 operation for these gaseous PAH's the oxidation catalyst efficiency was comparable to the better of either Mode 6 or 11 performance (gaseous acenaphthene, acenaphthylene, 2,6-dimethyl naphthalene, fluorine) or was better than both (gaseous anthracene, fluoranthene, phenanthrene, pyrene). This result is probably due to the much higher level (2 to 10 times) of these gaseous PAH's during Mode 22 compared to Modes 6 and 11.
- Engine-out brake specific PM emissions were lower during Mode 22 operation than during Modes 6 or 11. The oxidation catalyst reduced PM in both the "high" and "low" emission state. This is explained by the higher percent SOF in the Mode 22 PM that could be oxidized. Mode 6 and 11 PM were unaffected by the oxidation catalyst. The oxidation catalyst during any engine operating modes did not affect insoluble PM.
- Engine-out brake specific PM phase PAH emissions during Mode 22 operation were higher than for Mode 6 for ten compounds; comparable for six compounds; and lower for one compound. Compared to mode 11, Mode 22 brake specific PM phase PAH emissions were higher for six compounds; comparable for nine compounds; and lower for two compounds. During Mode 22 operation, the oxidation catalyst did not affect eleven of the PM phase PAH emissions, but did reduce emissions for six compounds. For the six compounds affected, the oxidation catalyst efficiency during Mode 22 was comparable to its efficiency during Modes 6 and 11. With the exception of indeno (1,2,3-cd) pyrene, the eleven PM phase PAH's not affected by the oxidation catalyst were also not affected by the oxidation catalyst during Modes 6 and 11 operation.



- Because Mode 22 is very low power the absolute emissions per unit operating time are low. However for emission test cycles with long idle periods, lower molecular weight species (HC, CO, aldehydes) could make a significant contribution to the total cycle emissions. Also, if the step changes in aftertreatment device efficiency observed in this study of low power operation are a common phenomenon, the variability of the emission test results will be high.

## 8.0 RECOMMENDATIONS

The previously demonstrated effect of the oxygenate compound blended into low sulfur diesel fuel on lowering both regulated and unregulated emissions did not appear to hold true at certain operating conditions when the engine was operated for low NO<sub>x</sub> emissions. In particular, Mode 22 operation, a transitional mode of operation, appeared to result in increased emissions with oxygenated fuels. These results may have been influenced by the fixed duration pilot fuel injection event. The sensitivity of emissions to the pilot fuel injection event for Mode 22 may warrant investigation.

To meet Tier 2 emission levels, engine out NO<sub>x</sub> emissions will need to be reduced, which will result in an increase in PM emissions. Thus, the use of a Diesel Particulate Filter (DPF) to meet Tier 2 PM emission levels will be required. The DPF will act as a trap that will periodically need regeneration to lower engine backpressure. The emission of toxicologically relevant compounds during DPF regeneration is not well understood. Also the emission of PAH compounds during engine cold start and warm up, due to prior accumulation of PM on a DPF, warrants investigation.

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## **APPENDIX A**

### **COLLECTION OF ALDEHYDE ON SOLID PHASE DNPH CARTRIDGES AND GASEOUS HYDROCARBONS IN TEDLAR BAGS USING A GAS METERING CART**

## **COLLECTION OF ALDEHYDE ON SOLID PHASE DNPH CARTRIDGES AND GASEOUS HYDROCARBONS IN TEDLAR BAGS USING A GAS METERING CART**

### **Leak Check**

- Close sampling point valves on tunnel and dilution air box.
- Aldehyde Sampling Cart - Attach the intake and suction lines together without a DNPH cartridge in line.
- Turn on the "Sampling" Switch and observe the digital flow meter. The flow should diminish to at least 0.20 L/min on the number 1 sample counter.
- Open sampling point valves (2 each) on tunnel and (1 each) on dilution air box. Attach 1 Tedlar sample bag each to the ASample≡ pump and the Abackground≡ air pump.
- Attach 1 each labeled DNPH aldehyde cartridge to the "Sample" side and the "background" side of the sampling cart. (Blue coded line for background(1) and Yellow coded line for sample(2)). Flows are regulated so that the sample flow rate is 5 times the background flow rate.

### **Start of Test:**

- In concert with the start of particulate sampling, begin timing the tests (30 min) with a stop watch. At start of test move the "sample" toggle switch 2 clicks upward. Simultaneously turn on the power strip to supply power to the bag sampling pumps.
- (The technician operating the particulate cart will give a "Start" sign.)
- After two minutes turn off the power to the "background" bag sampling pump.
- Sample with the DNPH cartridge and gas "sample" bag for 30 minutes.
- At some time during the test, record the barometric pressure, the LFE intake air temperature, and the ambient air temperatures. (These are displayed on the computer monitor on the test cell console.)

### **End of Test:**

- Move "sample" toggle switch to bottom position.
- Turn off power to the bag sampling pump.
- Record the numbers on both top and bottom digital flow meters.
- Disconnect Sample Bag from Pump.
- Return background pump line switch to the Aon≡ position.
- As soon as practical, deliver the ASample≡ bag to DER GC lab.
- Leave background bag attached until end of test day. (Two minutes for each test.)
- Remove DNPH Sample Cartridge from flow stream cap ends and verify correct label.
- At end of test session, place the aggregate of DNPH cartridges in a zip-lock bag and deliver to DER lab #2 small refrig., under lab bench near vent hood.

## **REVISION 1**

### **COLLECTION OF ALDEHYDES ON SOLID PHASE DNPH CARTRIDGES AND GASEOUS HYDROCARBONS IN TEDLAR BAGS USING GAS METERING CART**

#### **Revision 3/09/00**

Due to overloading of some of the aldehyde cartridges,( using up all of the DNPH reagent), the sampling regime was modified as follows:

#### **Zero Time**

- Start Aldehyde Cart pumps, ( no cartridges installed)
- Start Bag pumps

#### **At 2 minutes**

- Stop background bag pump
- Stop Aldehyde cart pumps
- Install cartridges, (sample and background)
- (this 2 minutes purges the sample lines with current sample)

#### **At 3 minutes**

- Start aldehyde cart pumps

#### **At 8 minutes**

- Close toggle valve to aldehyde “sample” cartridge.
- Read flow totalizer for “sample”
- Remove “sample” cartridge from flow stream
- ( 5-minute “sample” collection)

#### **At 30 minutes**

- Stop aldehyde cartridge pumps
- Stop “sample” bag pump
- Read flow totalizer for Background
- Remove background cartridge from flow stream, (set aside to reinstall 2 minutes into next test)
- Remove “sample bag” and transport to the chem. lab for analyses.

## **APPENDIX B**

### **Mode 6 Operation Test Results**



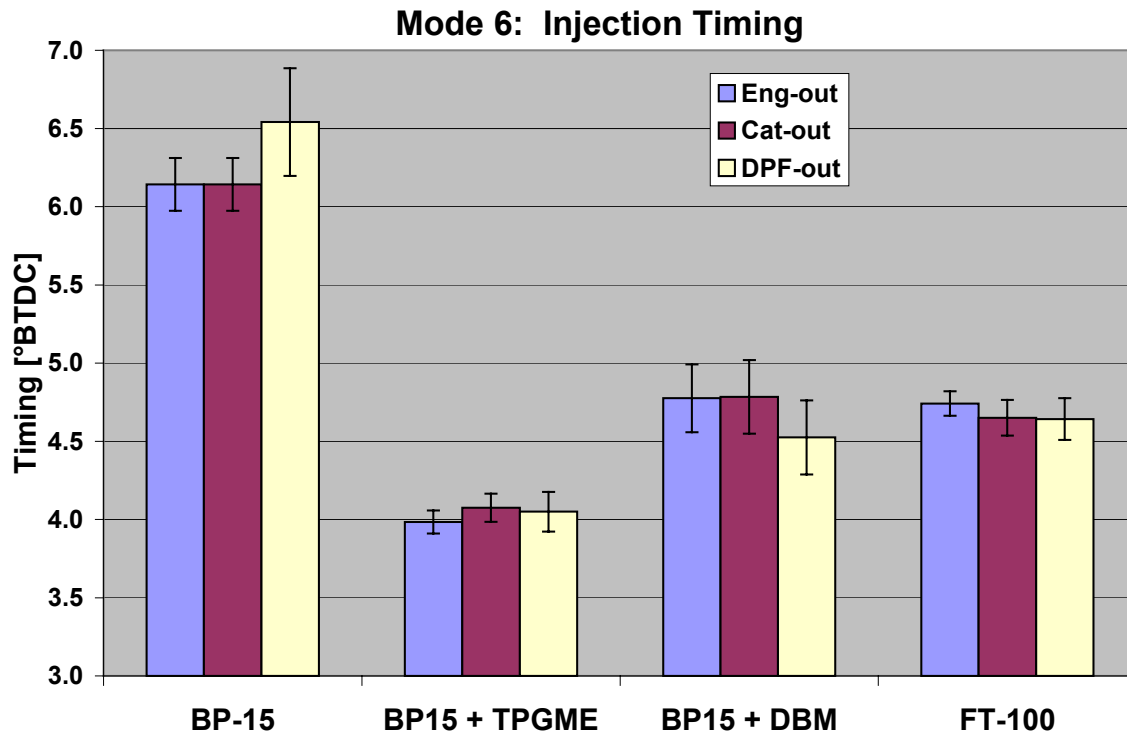


Figure B-1. Injection Timing by Fuel Type, Mode 6

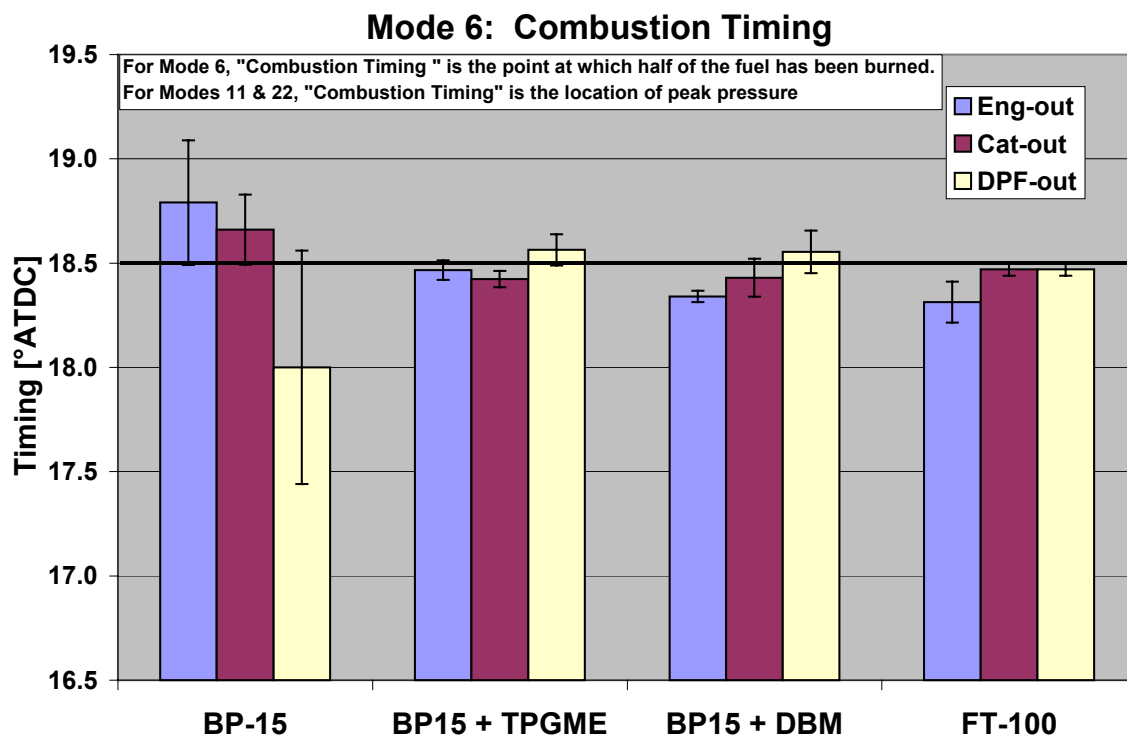


Figure B-2. Combustion Timing by Fuel Type, Mode 6

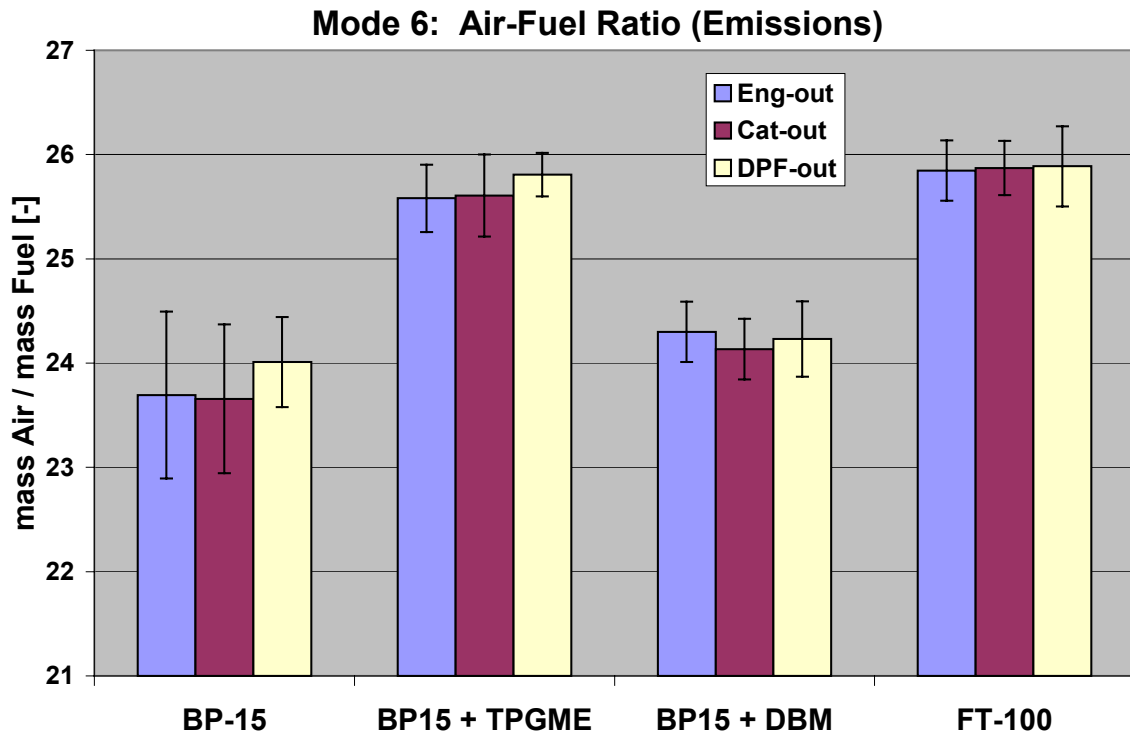


Figure B-3. Emissions Air-Fuel Ratio by Fuel Type, Mode 6

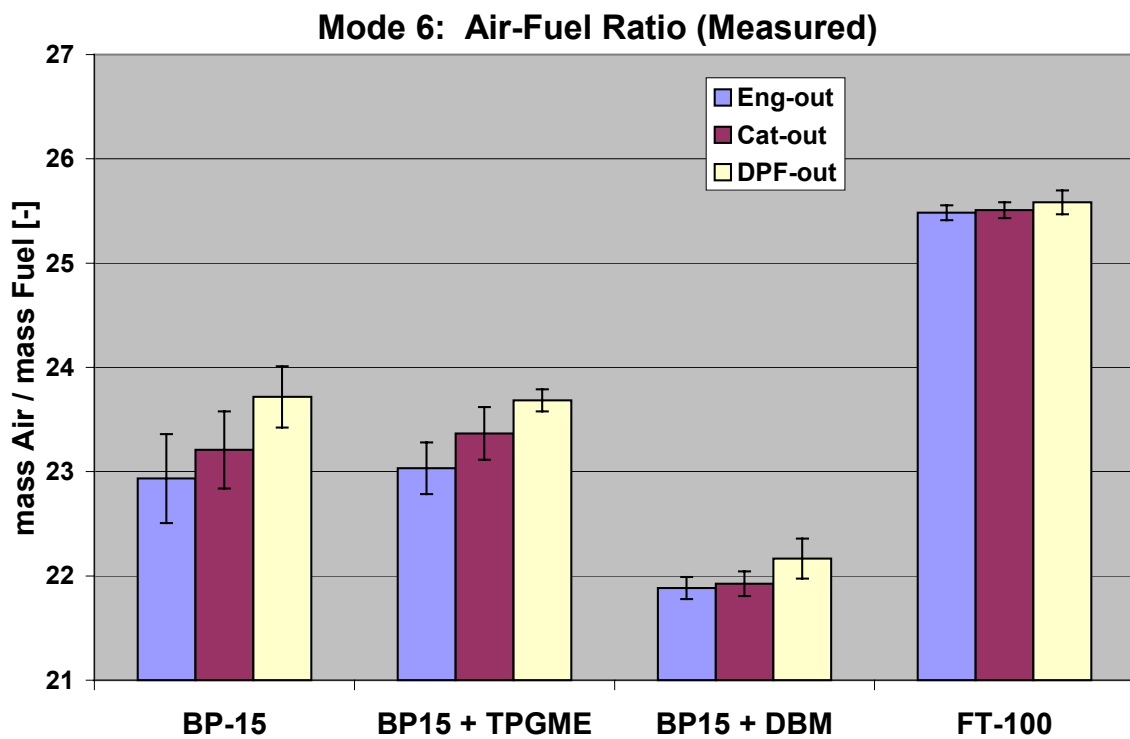


Figure B-4. Measured Air-Fuel Ratio by Fuel Type, Mode 6

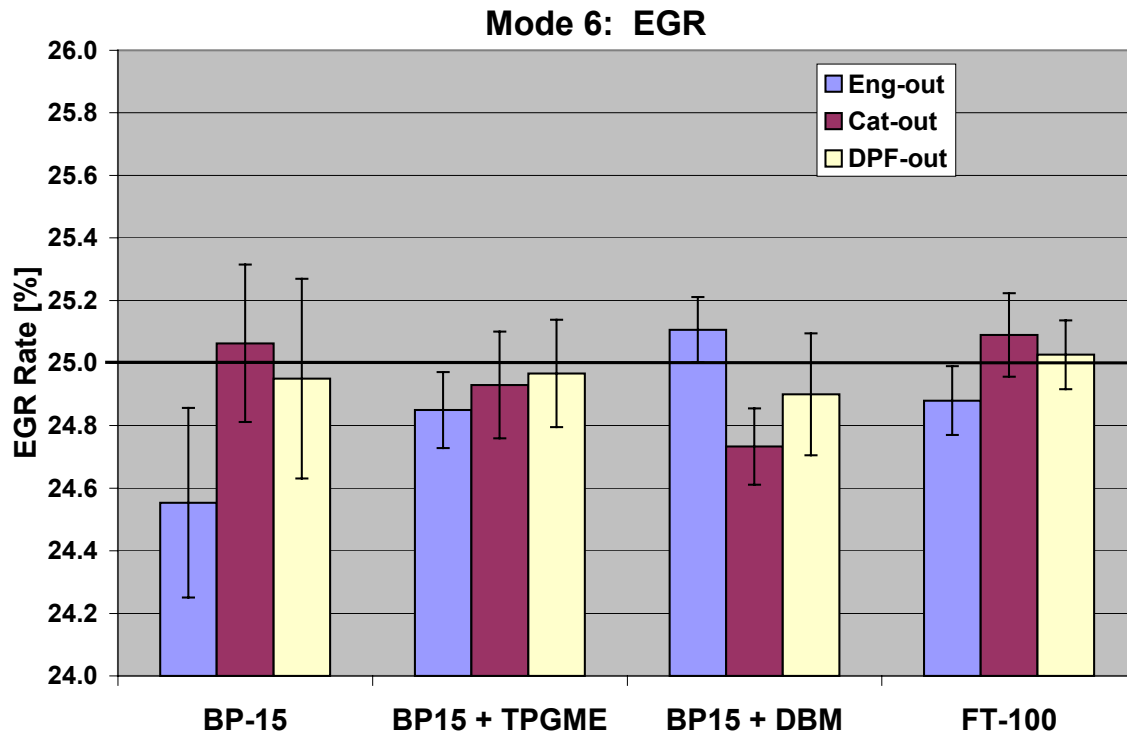


Figure B-5. EGR Rate by Fuel Type, Mode 6

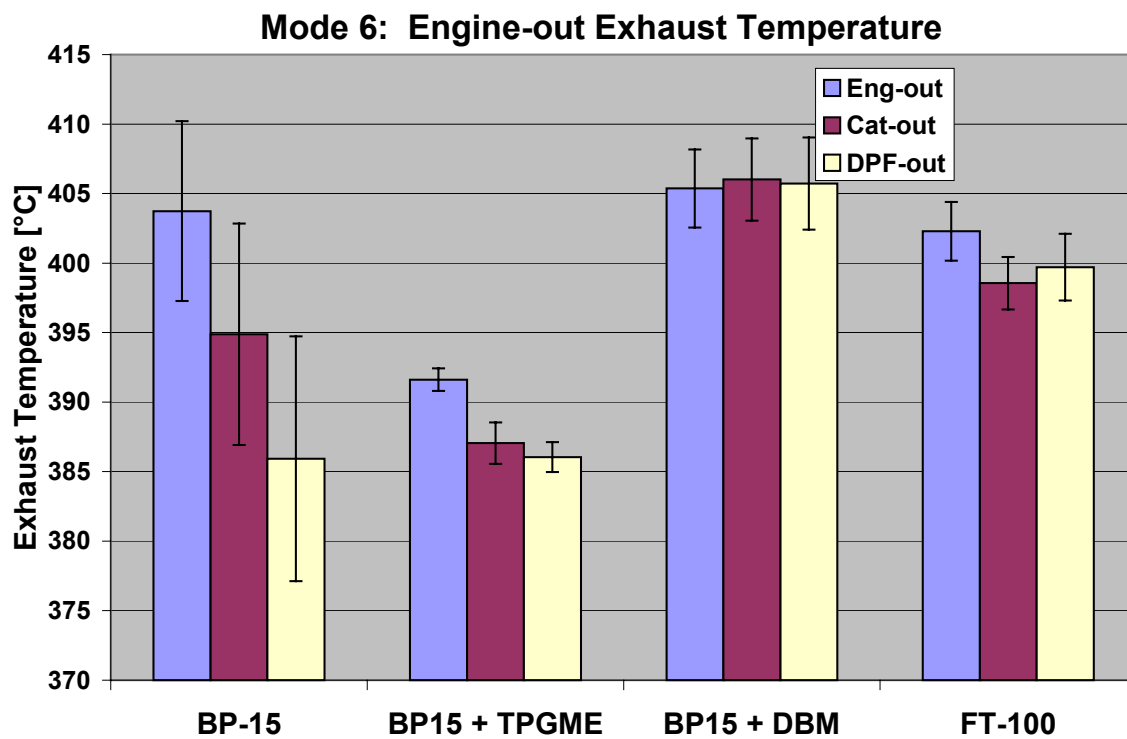


Figure B-6. Engine-Out Exhaust Temperature by Fuel Type, Mode 6

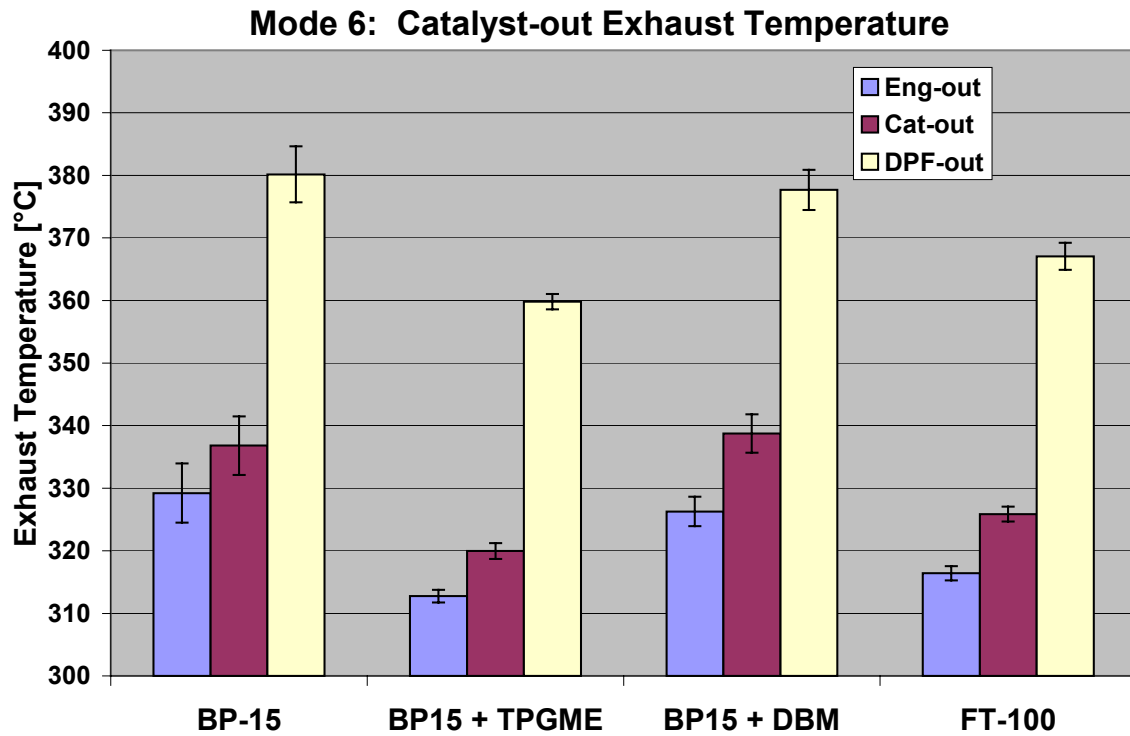


Figure B-7. Catalyst-Out Exhaust Temperature by Fuel Type, Mode 6

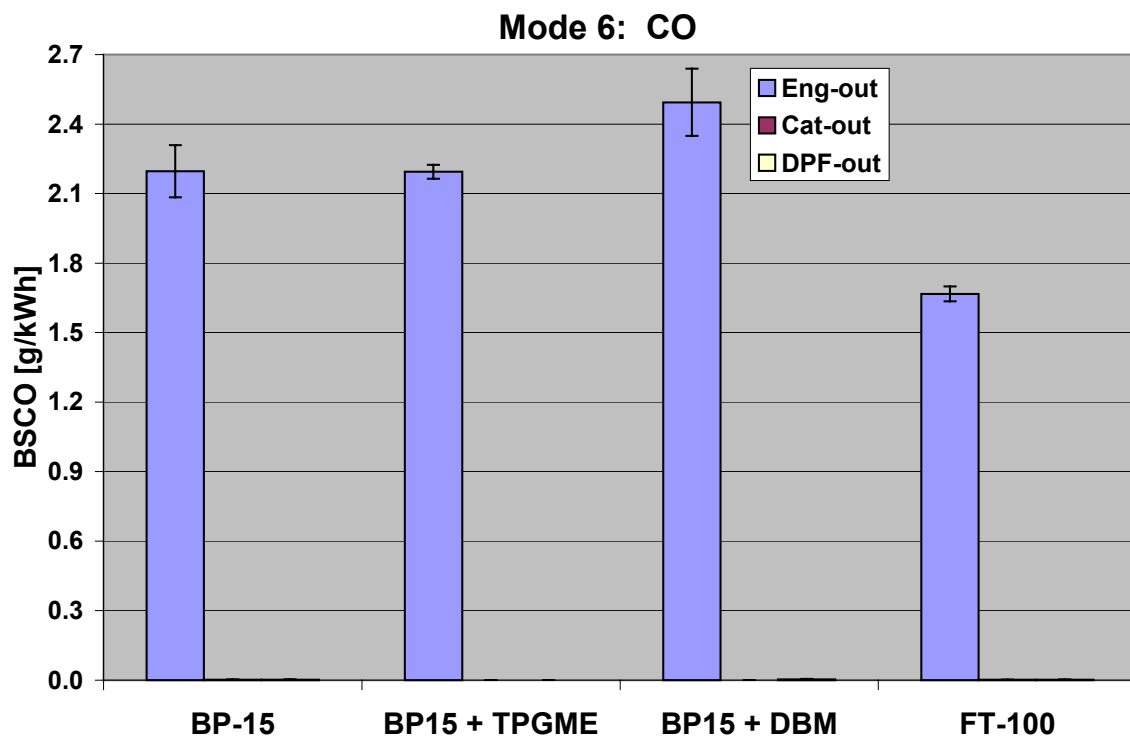


Figure B-8. Carbon Monoxide Emissions by Fuel Type, Mode 6

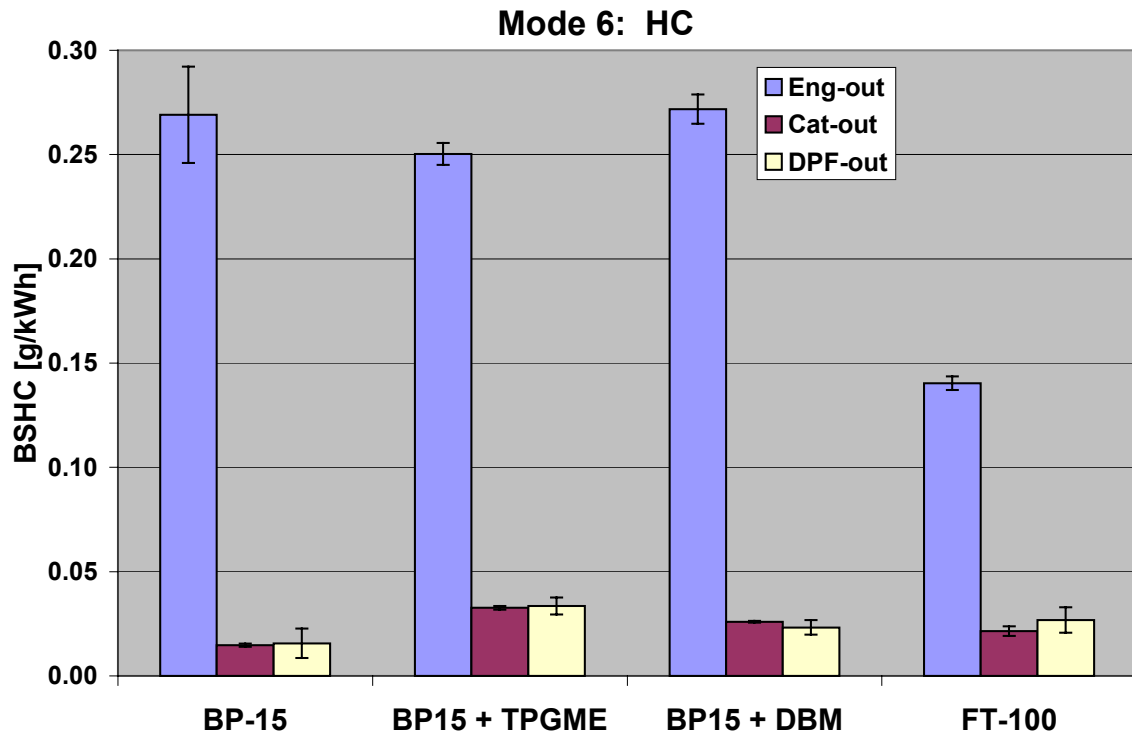


Figure B-9. Hydrocarbon Emissions by Fuel Type, Mode 6

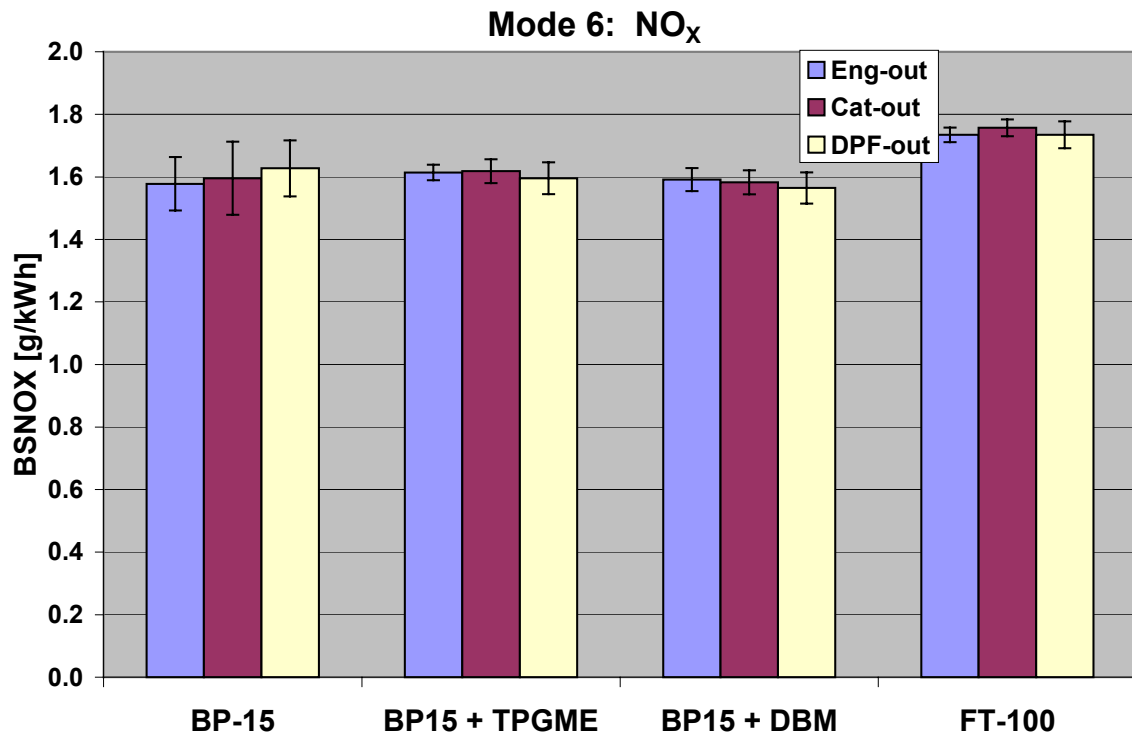


Figure B-10. Nitrogen Oxides Emissions by Fuel Type, Mode 6

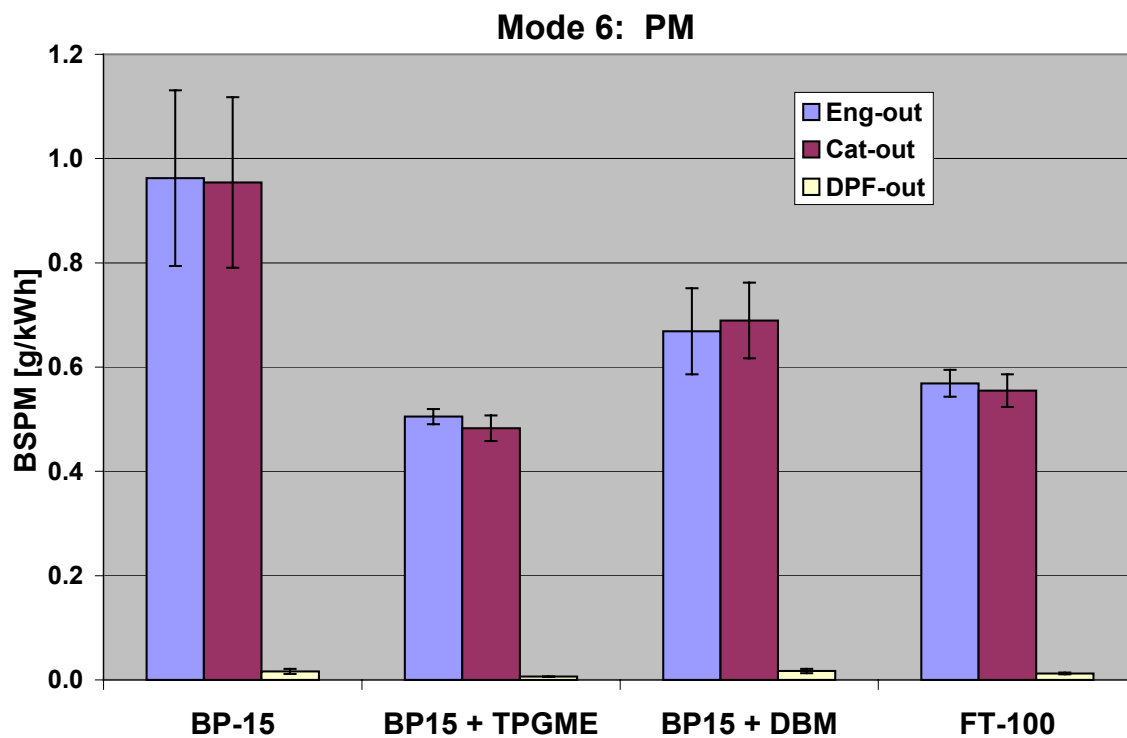


Figure B-11. Particulate Matter Emissions by Fuel Type, Mode 6

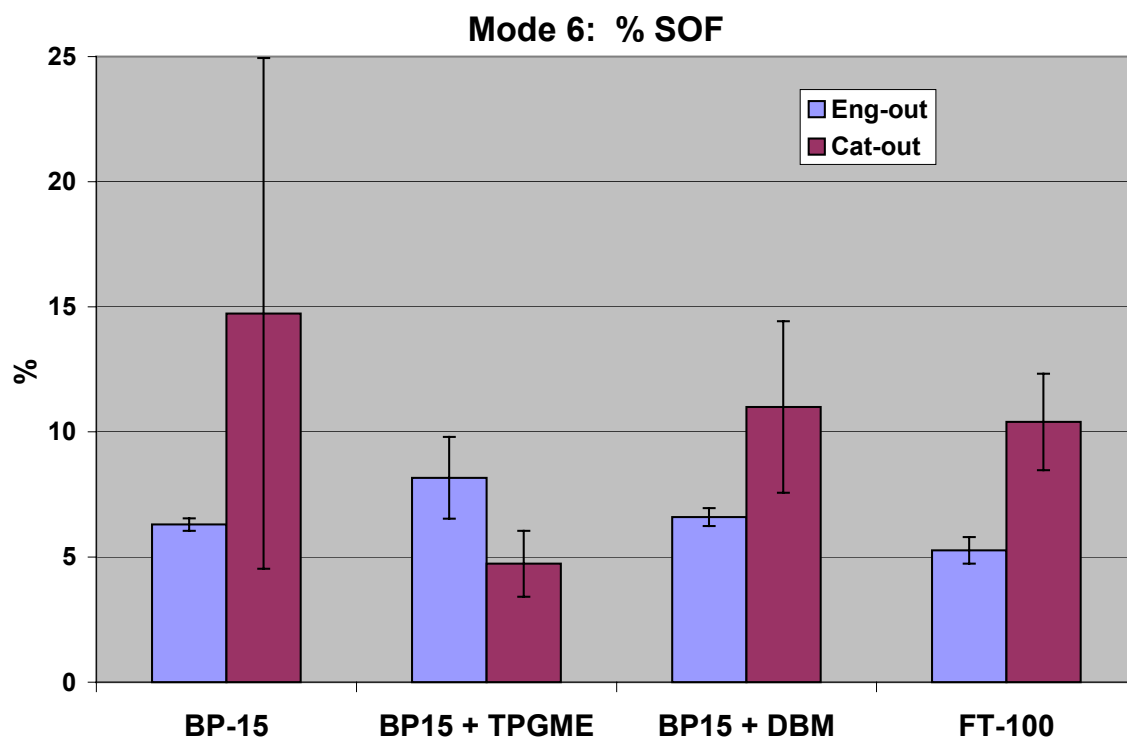


Figure B-12. Percent Soluble Organic Fraction by Fuel Type, Mode 6

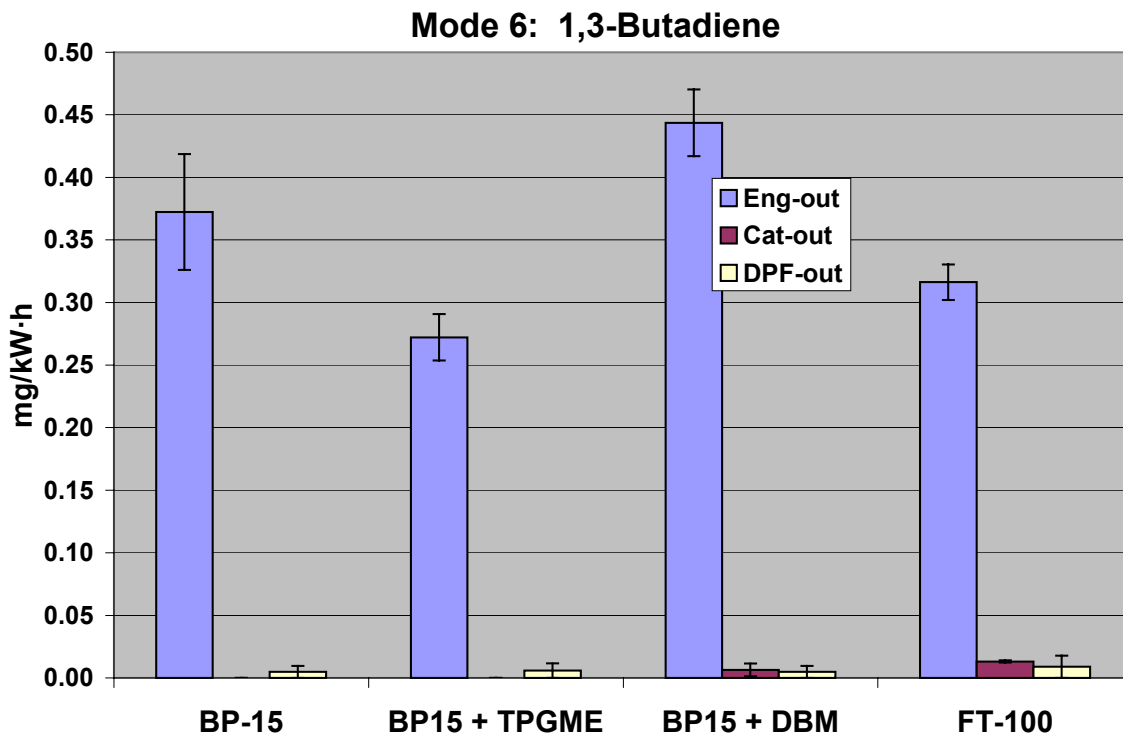


Figure B-13. 1,3-Butadiene Emissions by Fuel Type, Mode 6

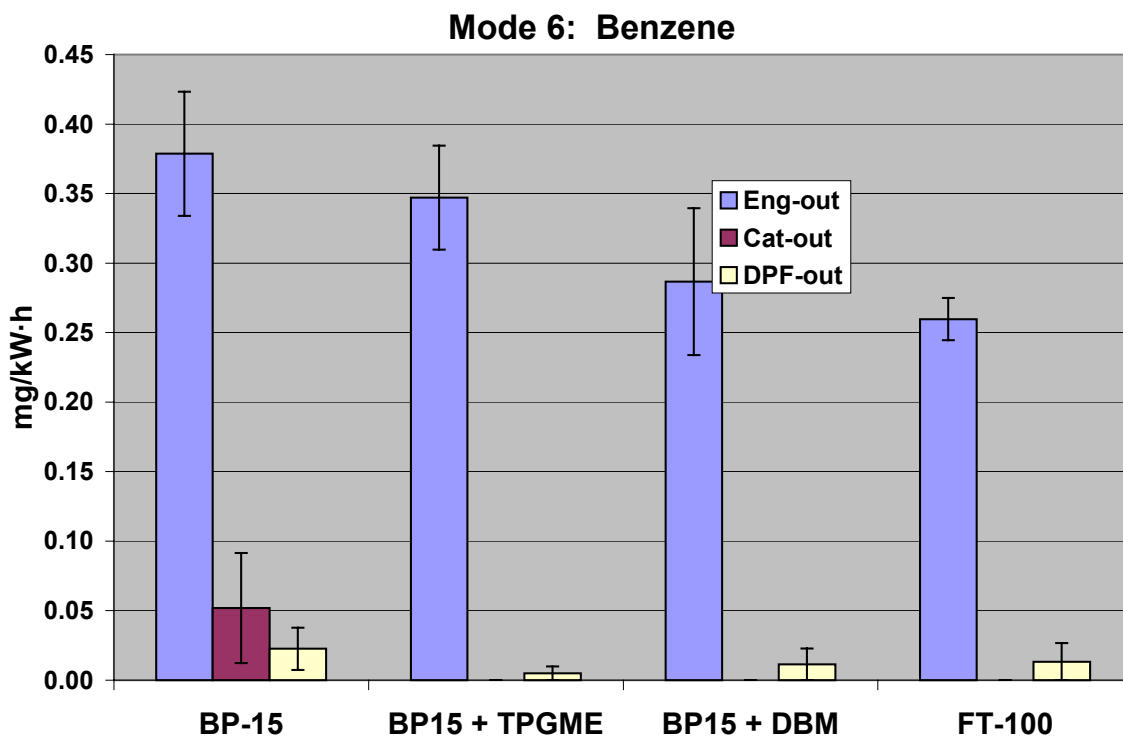


Figure B-14. Benzene Emissions by Fuel Type, Mode 6

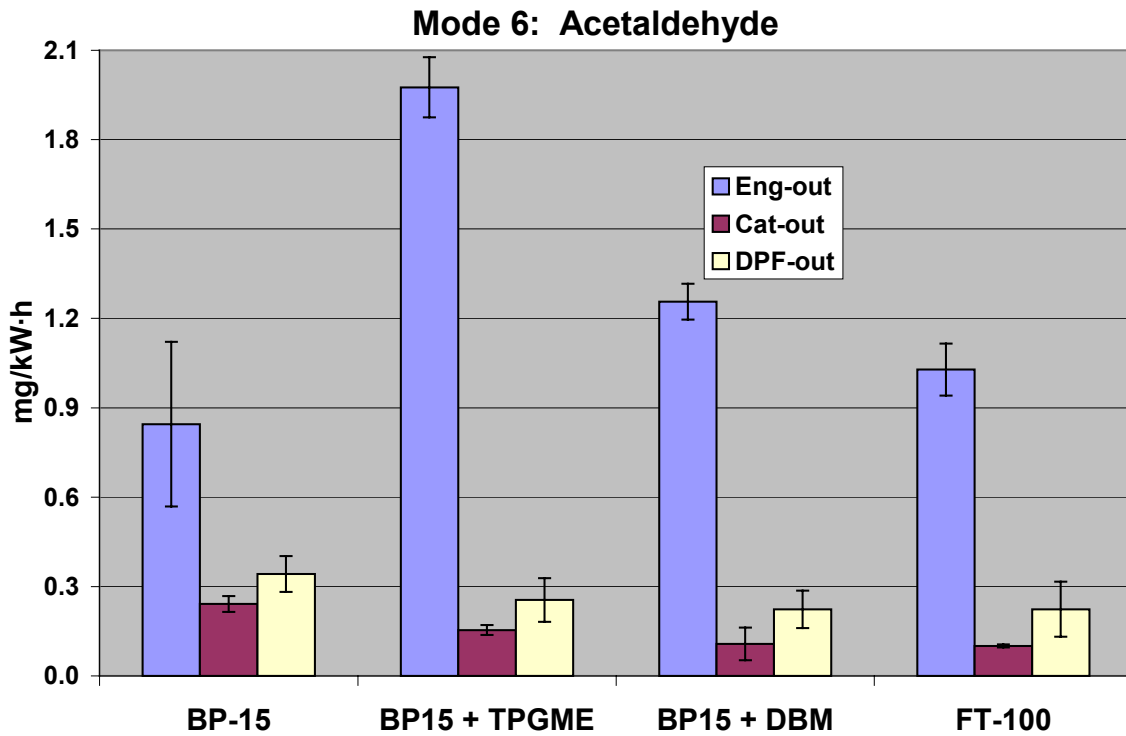


Figure B-15. Acetaldehyde Emissions by Fuel Type, Mode 6

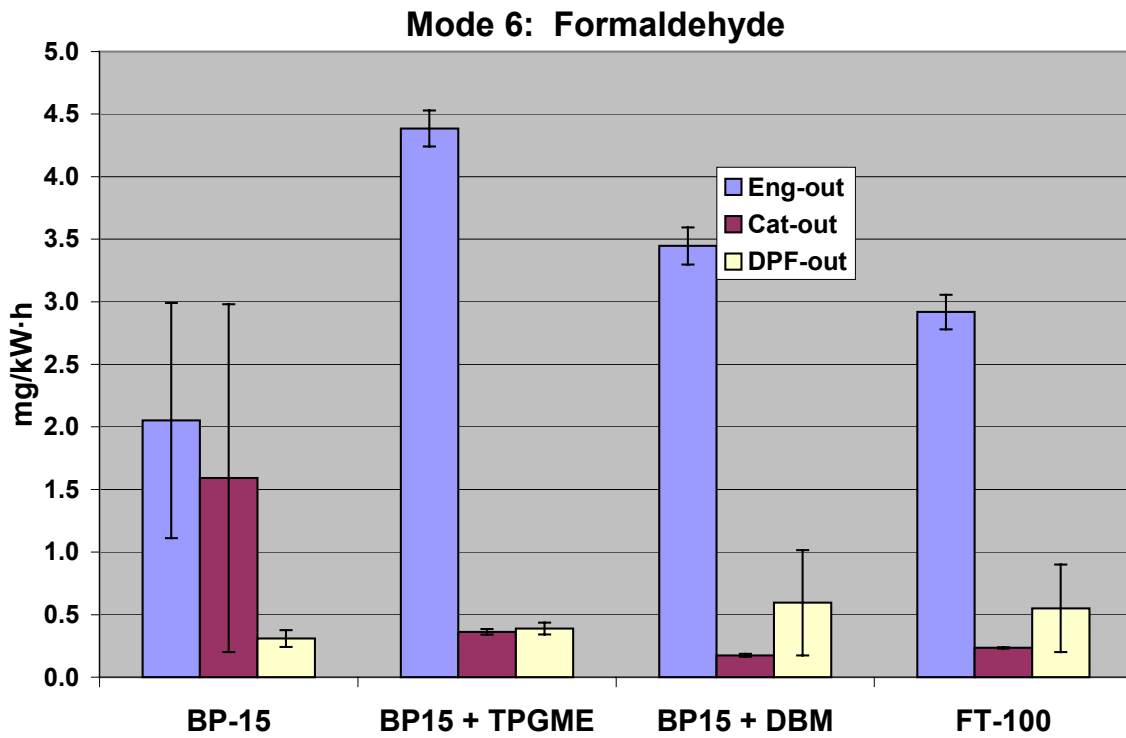


Figure B-16. Formaldehyde Emissions by Fuel Type, Mode 6



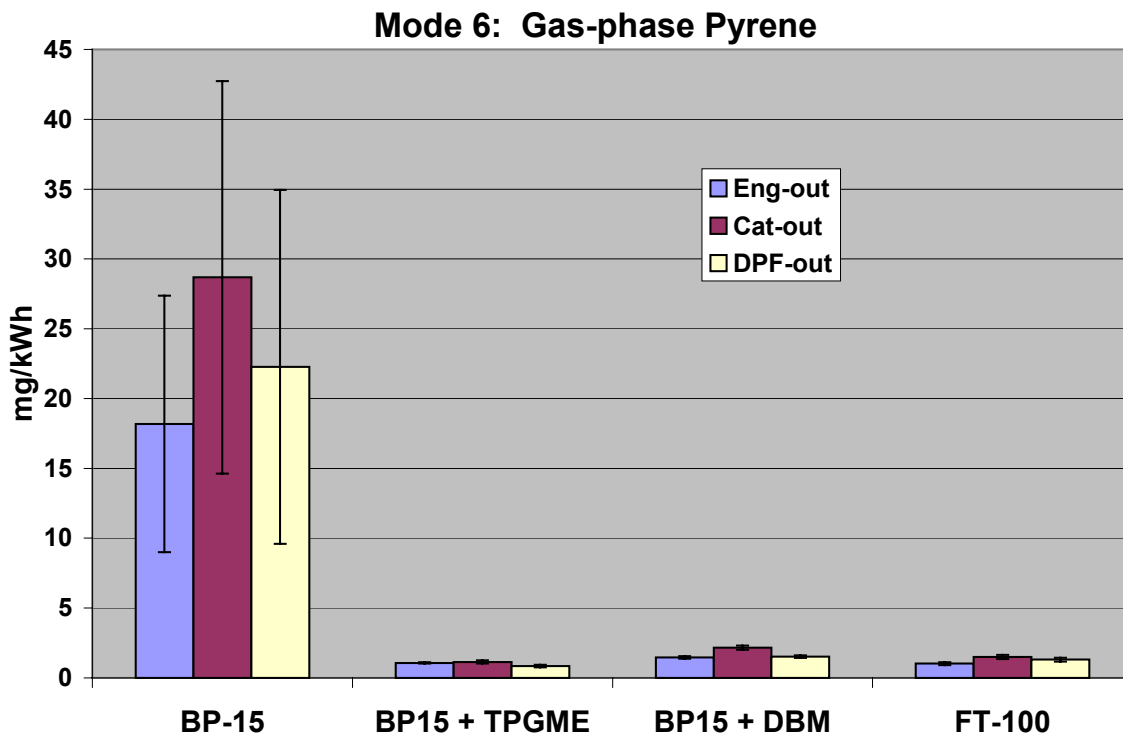


Figure B-17. Gas-Phase Pyrene Emissions by Fuel Type, Mode 6

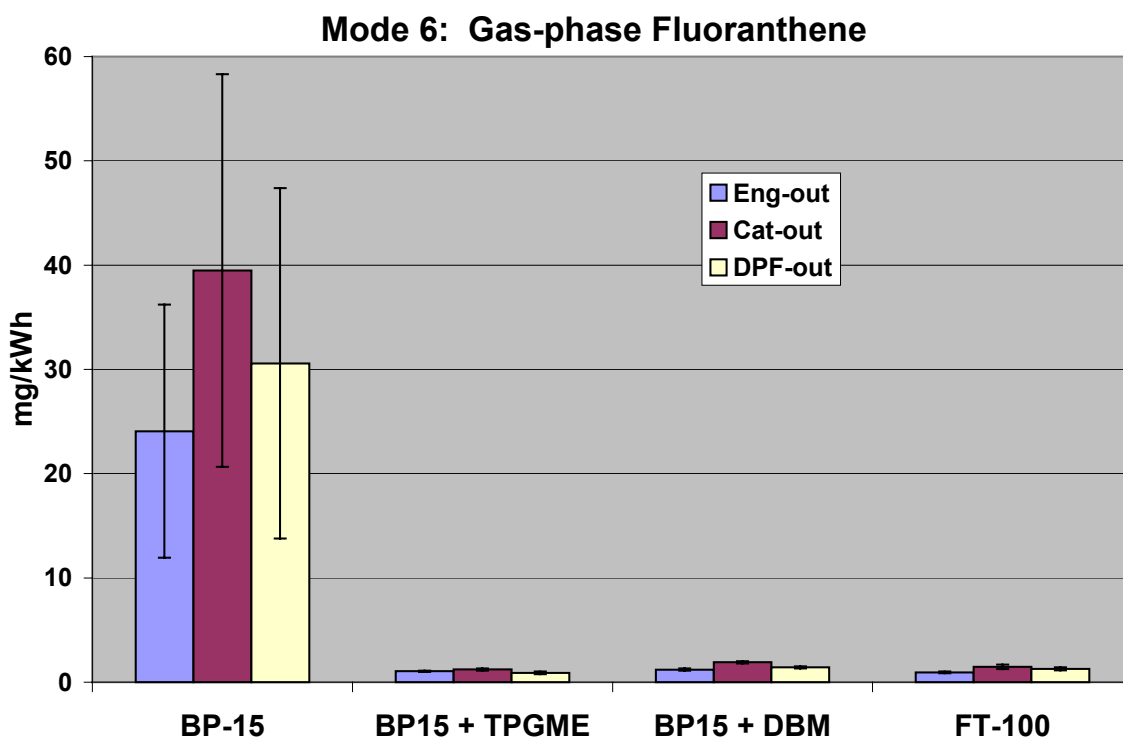


Figure B-18. Gas-Phase Fluoranthene Emissions by Fuel Type, Mode 6

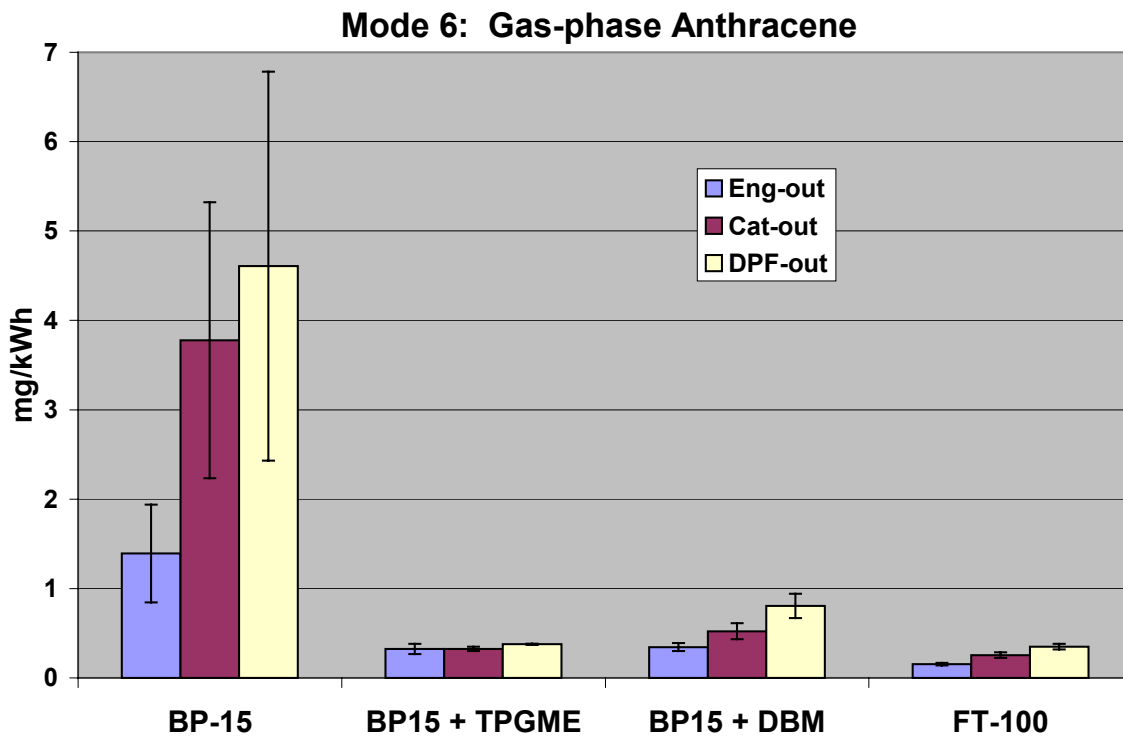


Figure B-19. Gas-Phase Anthracene Emissions by Fuel Type, Mode 6

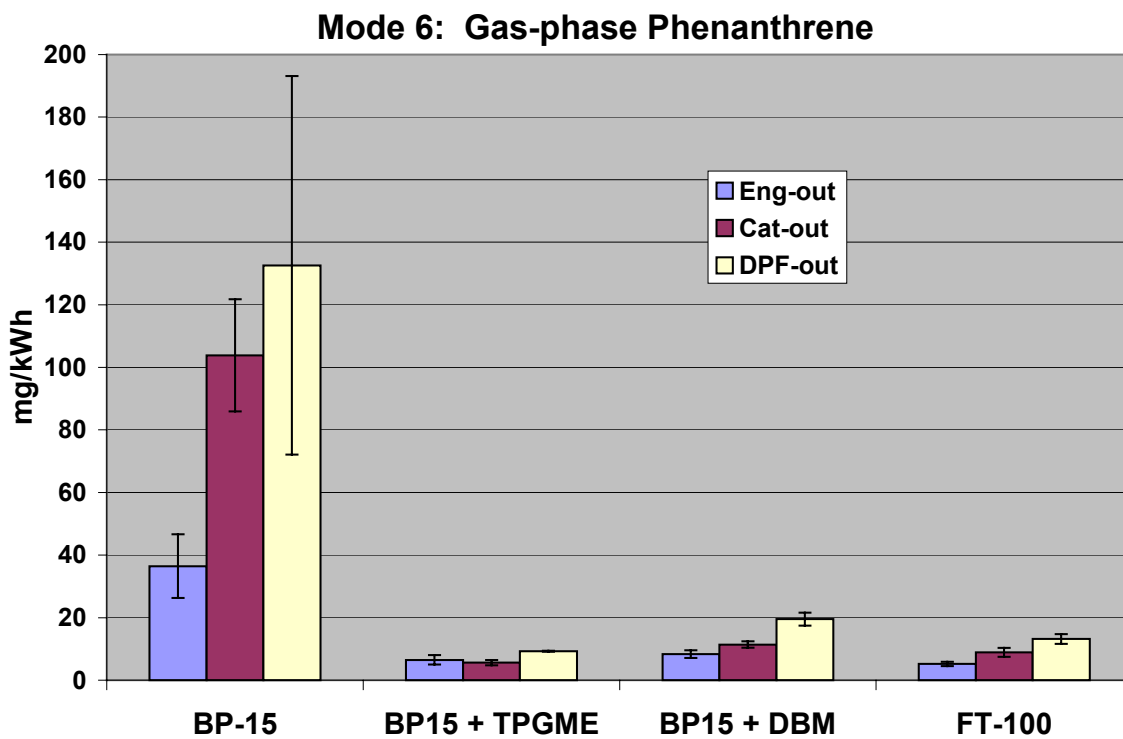


Figure B-20. Gas-Phase Phenanthrene Emissions by Fuel Type, Mode 6

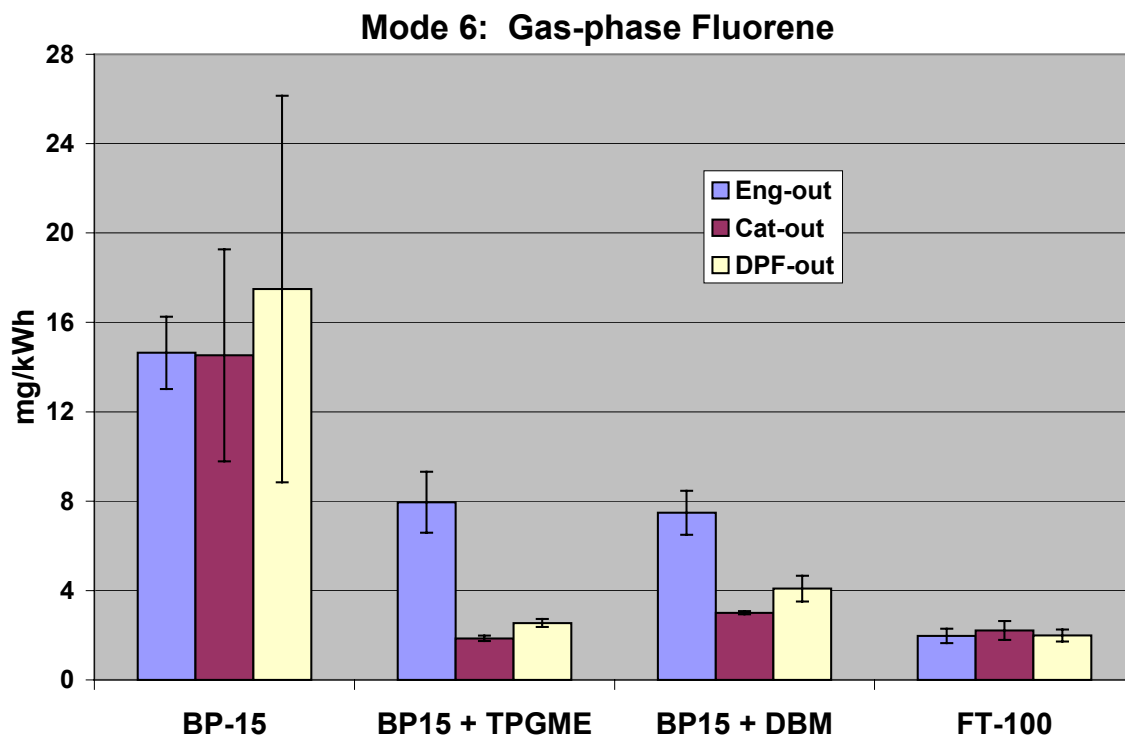


Figure B-21. Gas-Phase Fluorene Emissions by Fuel Type, Mode 6

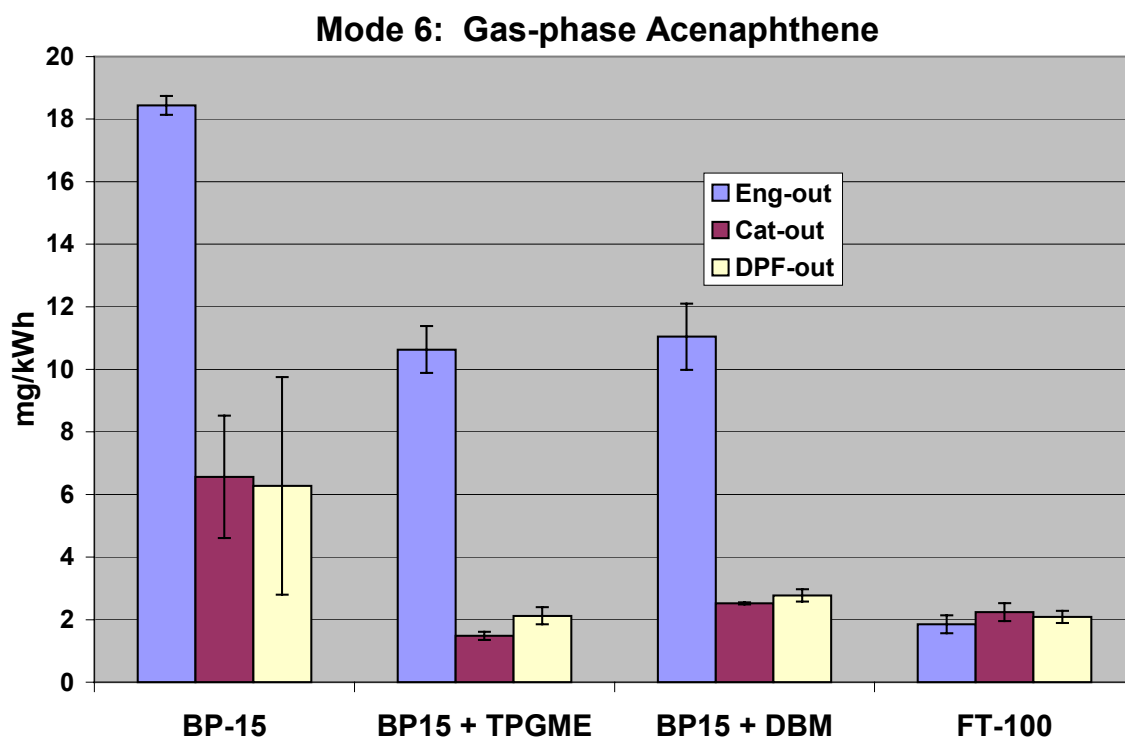


Figure B-22. Gas-Phase Acenaphthene Emissions by Fuel Type, Mode 6

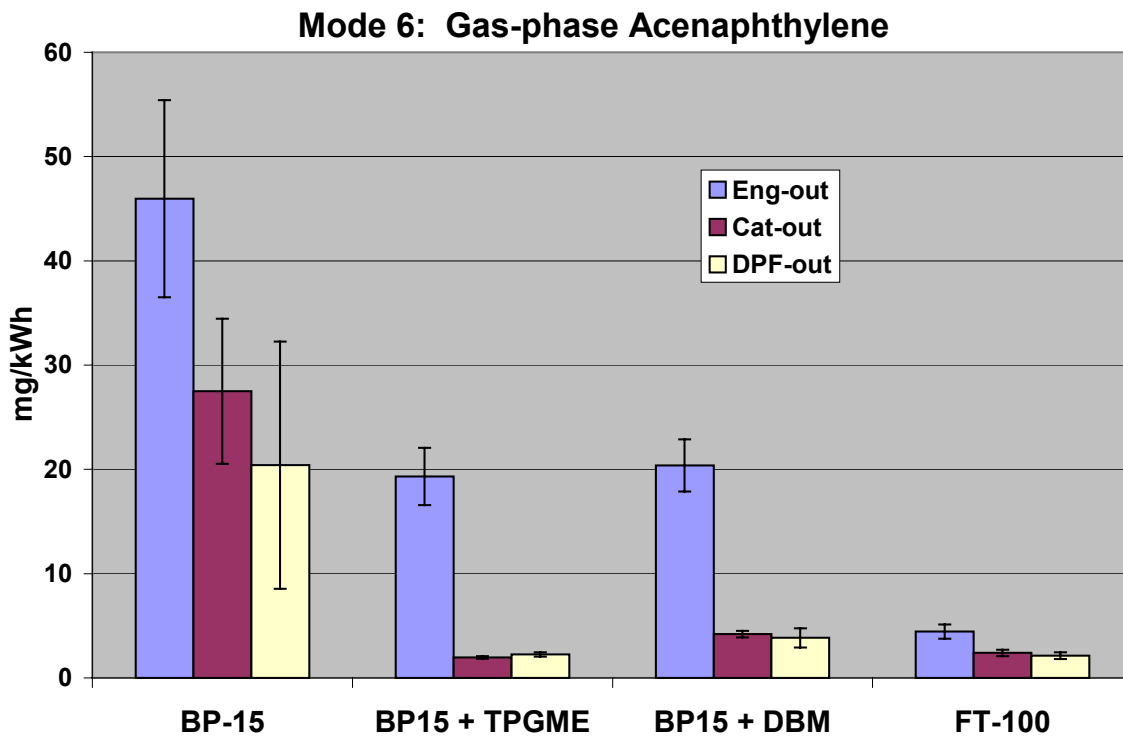


Figure B-23. Gas-Phase Acenaphthylene Emissions by Fuel Type, Mode 6

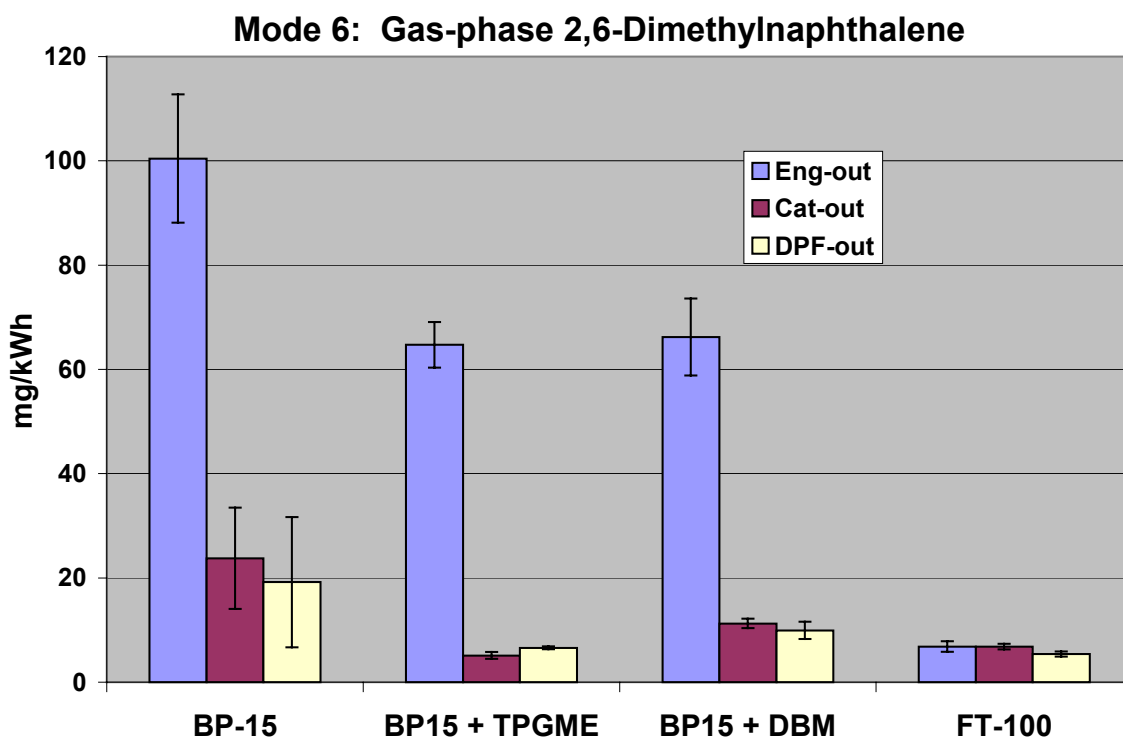


Figure B-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions by Fuel Type, Mode 6

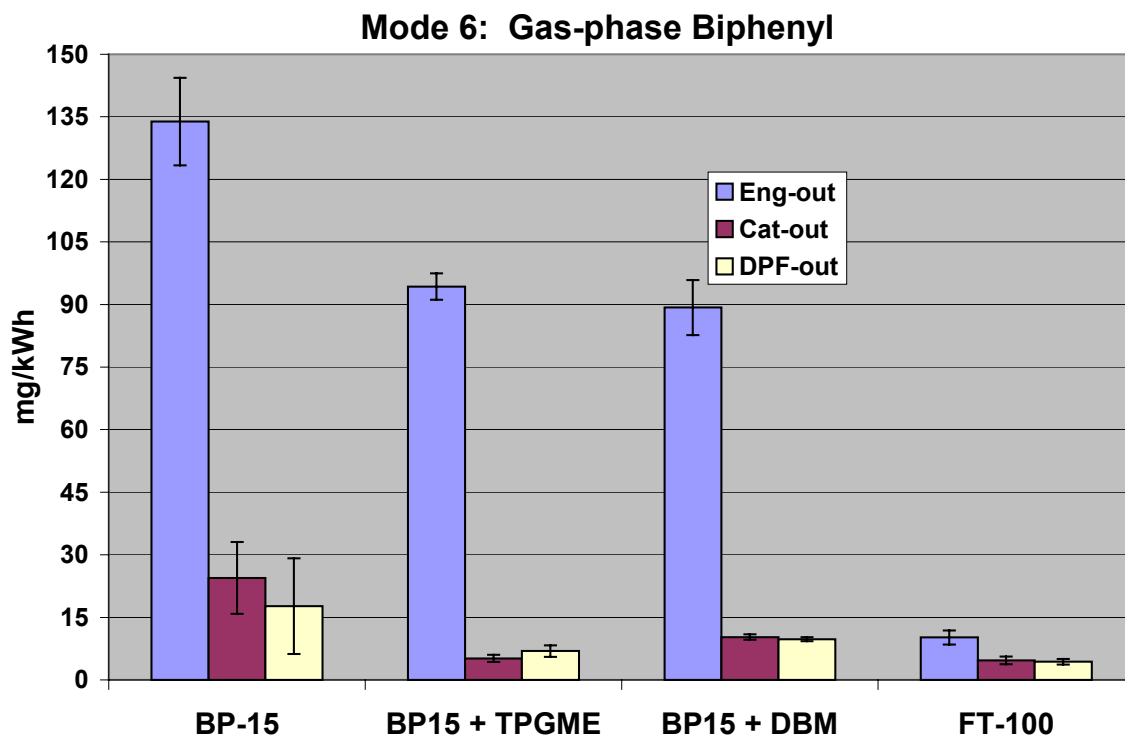


Figure B-25. Gas-Phase Biphenyl Emissions by Fuel Type, Mode 6

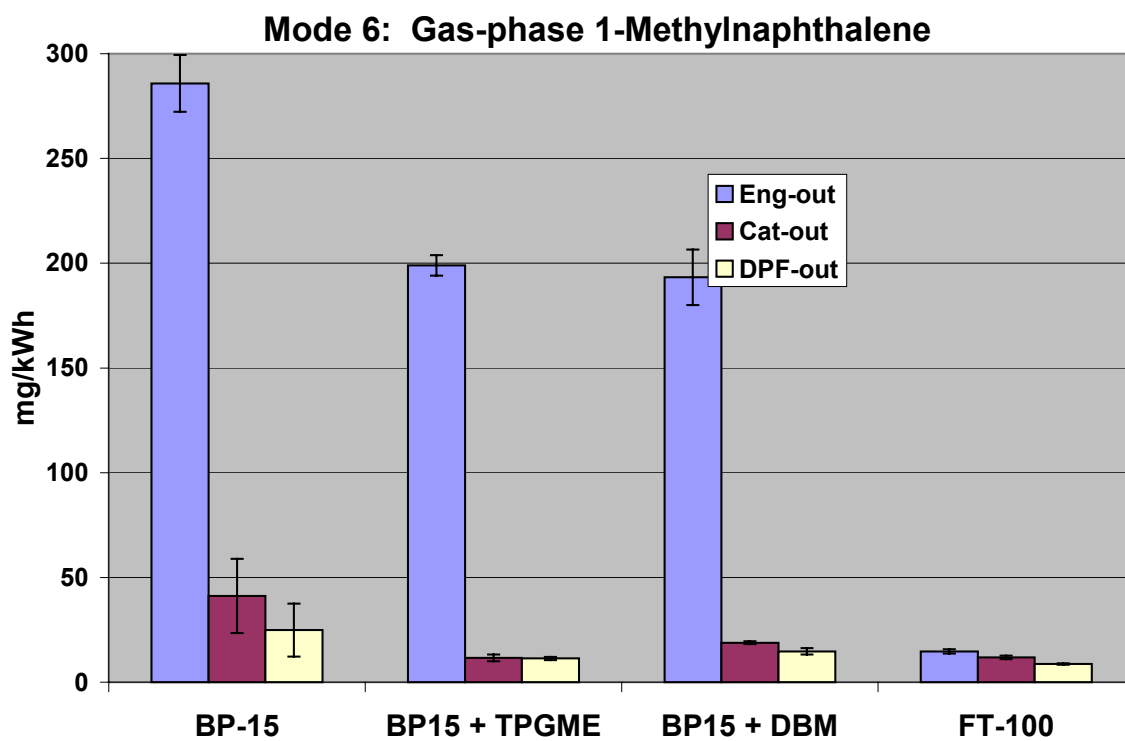


Figure B-26. Gas-Phase 1-Methylnaphthalene Emissions by Fuel Type, Mode 6

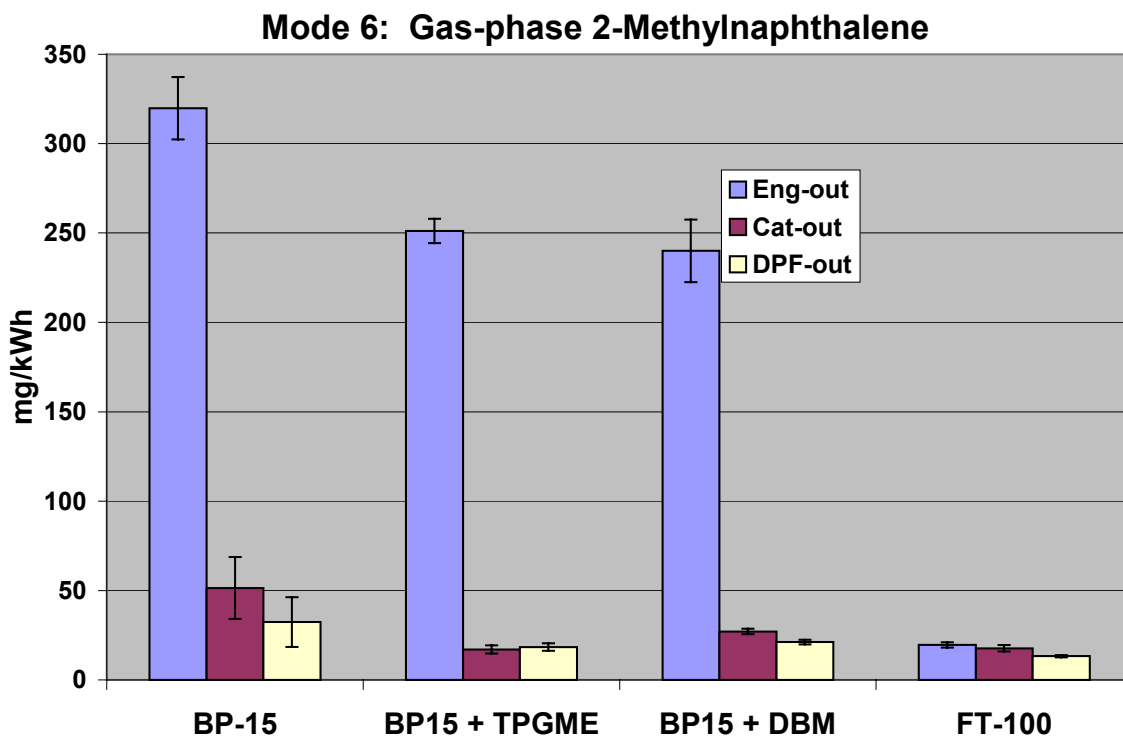


Figure B-27. Gas-Phase 2-Methylnaphthalene Emissions by Fuel Type, Mode 6

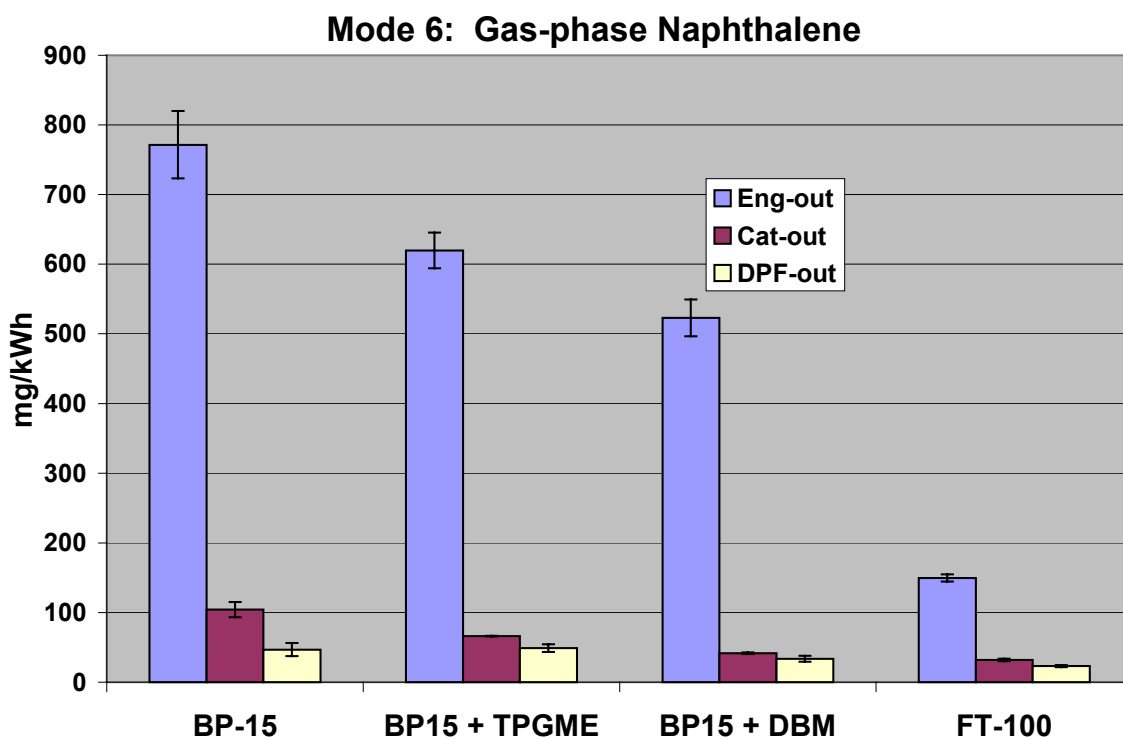


Figure B-28. Gas-Phase Naphthalene Emissions by Fuel Type, Mode 6

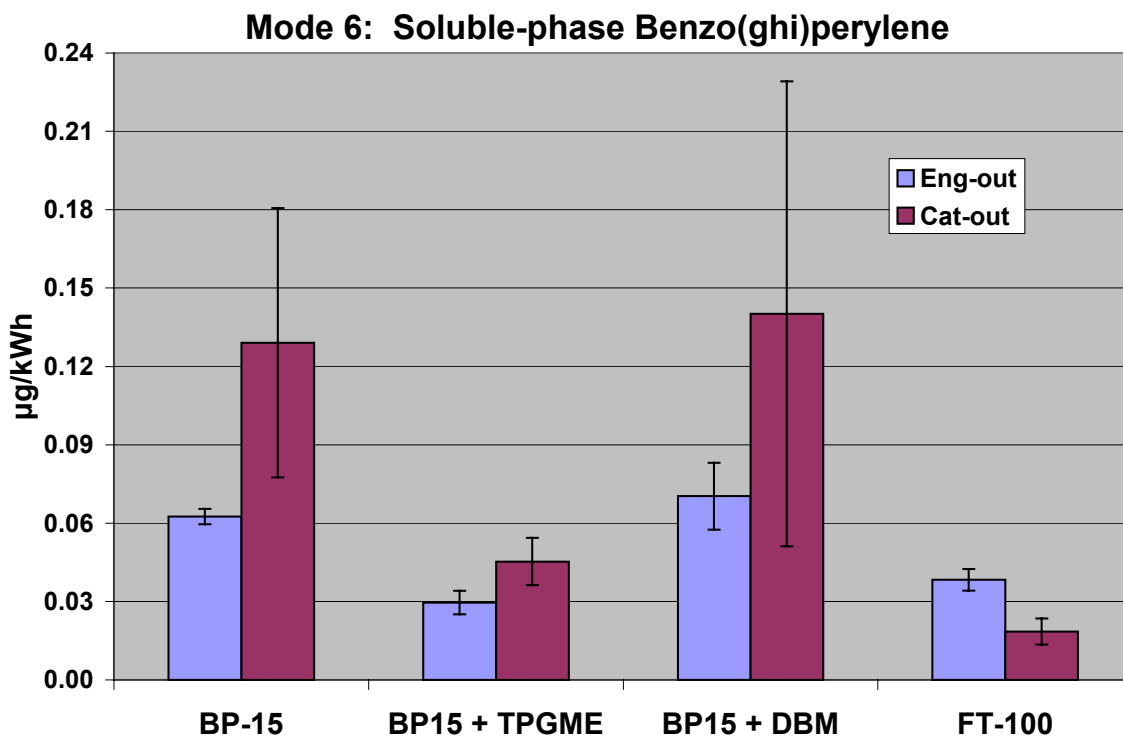


Figure B-29. Soluble-Phase Benzo(ghi)perylene Emissions by Fuel Type, Mode 6

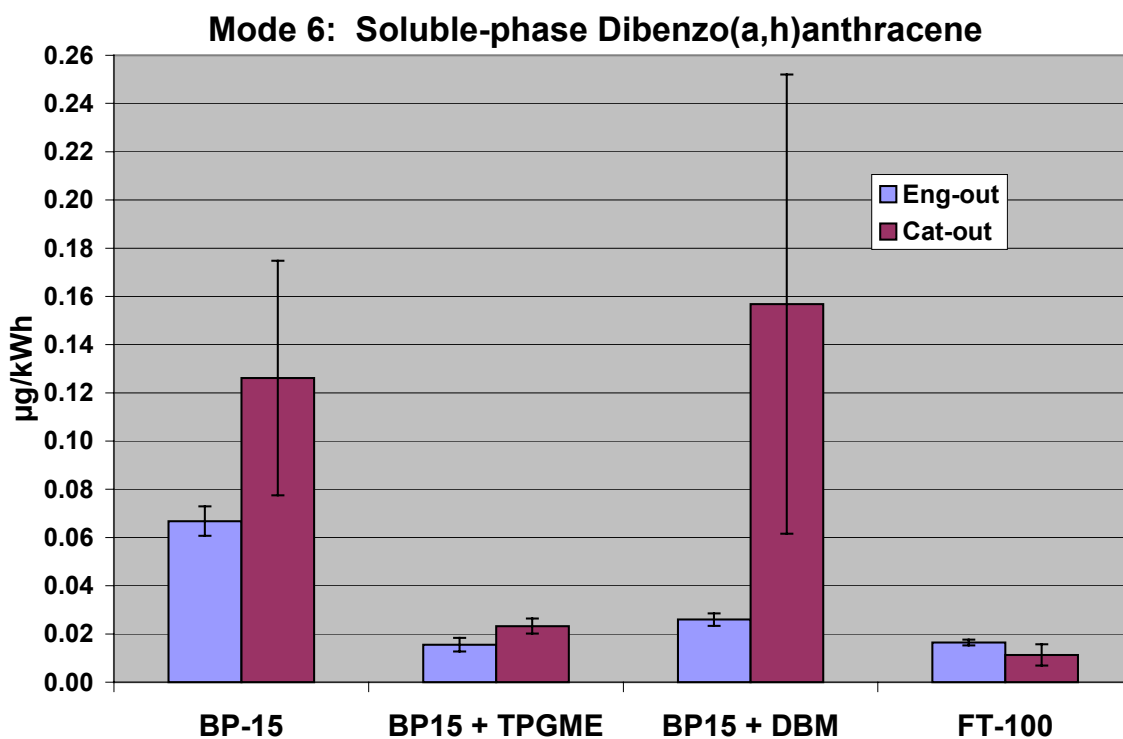


Figure B-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions by Fuel Type, Mode 6

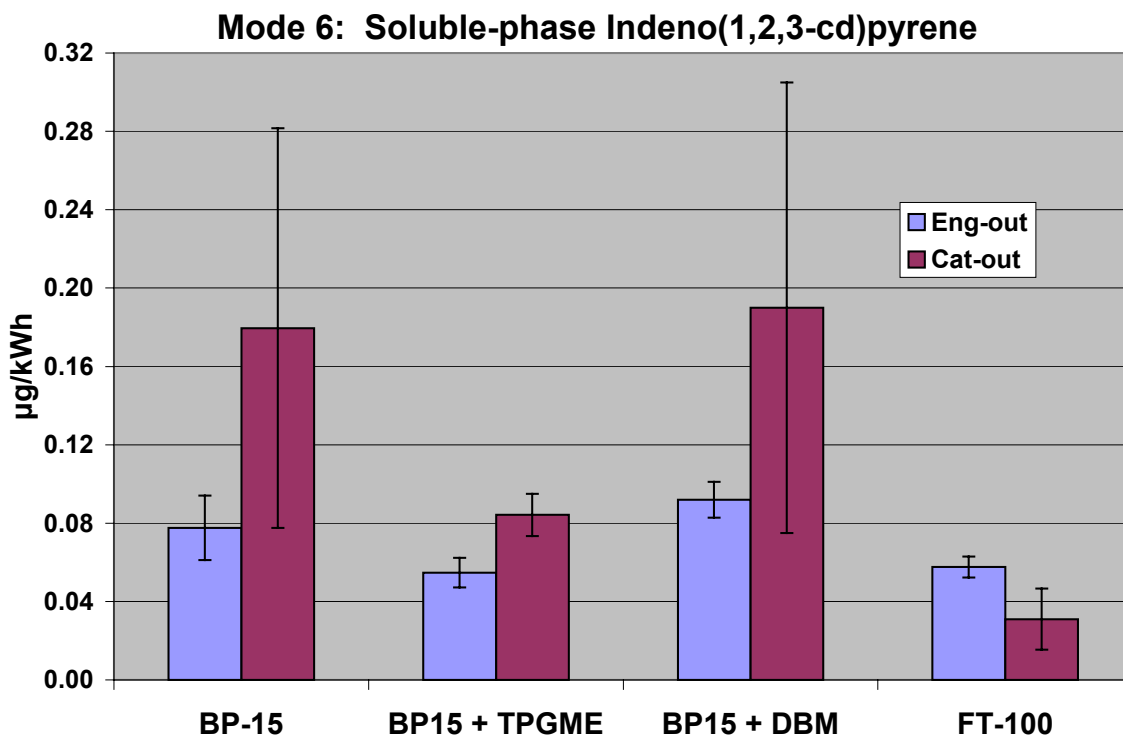


Figure B-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions by Fuel Type, Mode 6

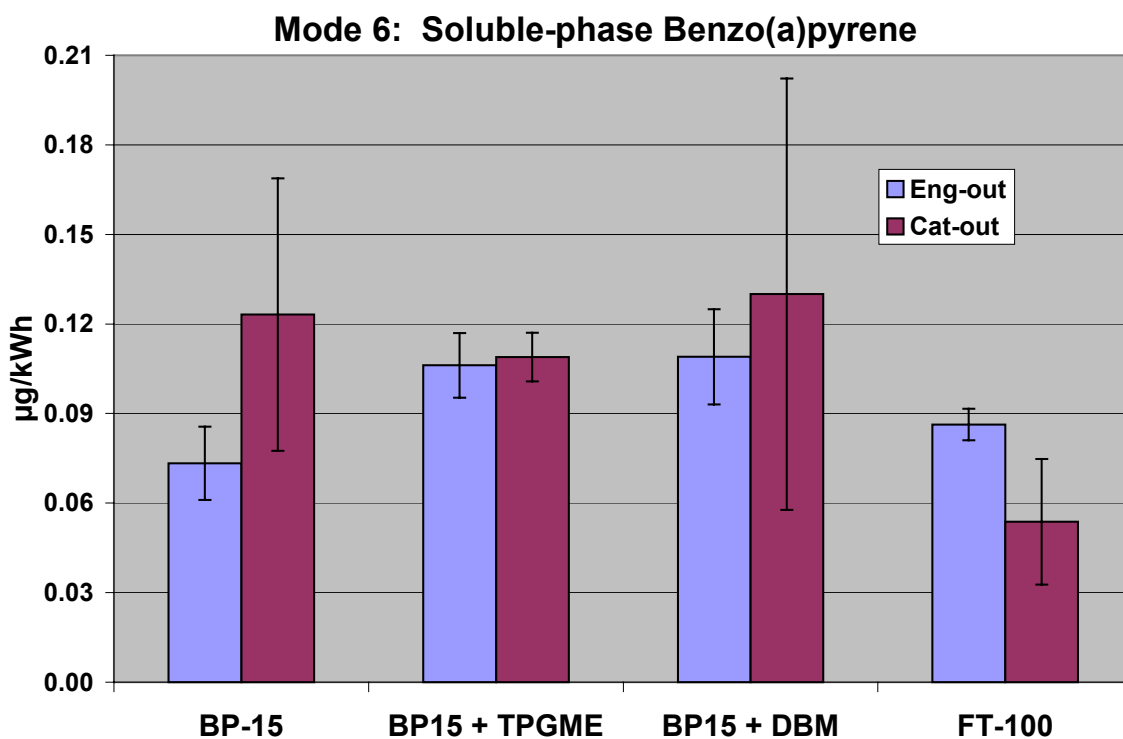


Figure B-32. Soluble-Phase Benzo(a)pyrene Emissions by Fuel Type, Mode 6



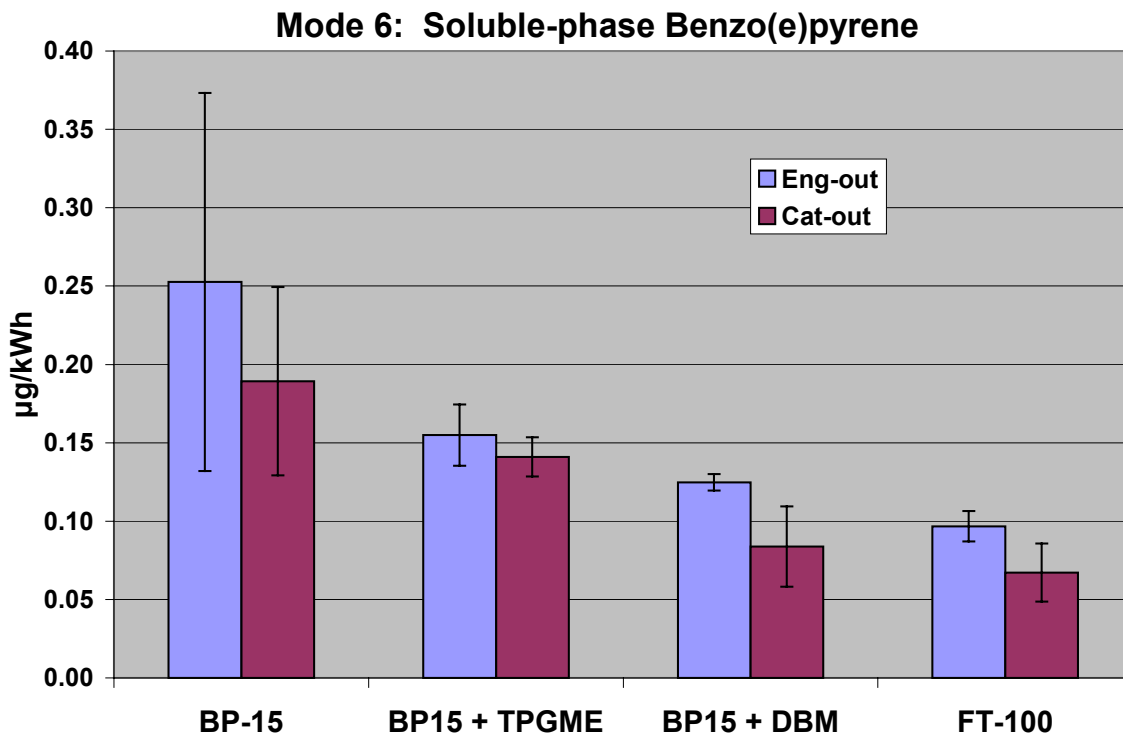


Figure B-33. Soluble-Phase Benzo(e)pyrene Emissions by Fuel Type, Mode 6

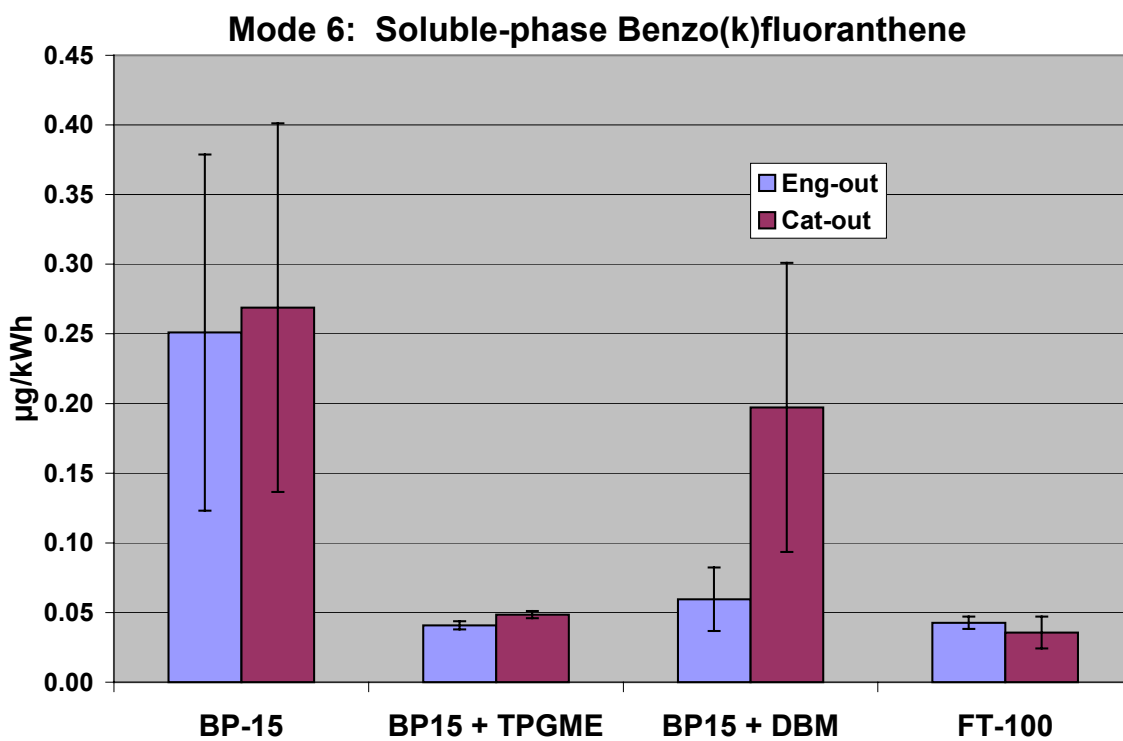


Figure B-34. Soluble-Phase Benzo(k)fluoranthene Emissions by Fuel Type, Mode 6

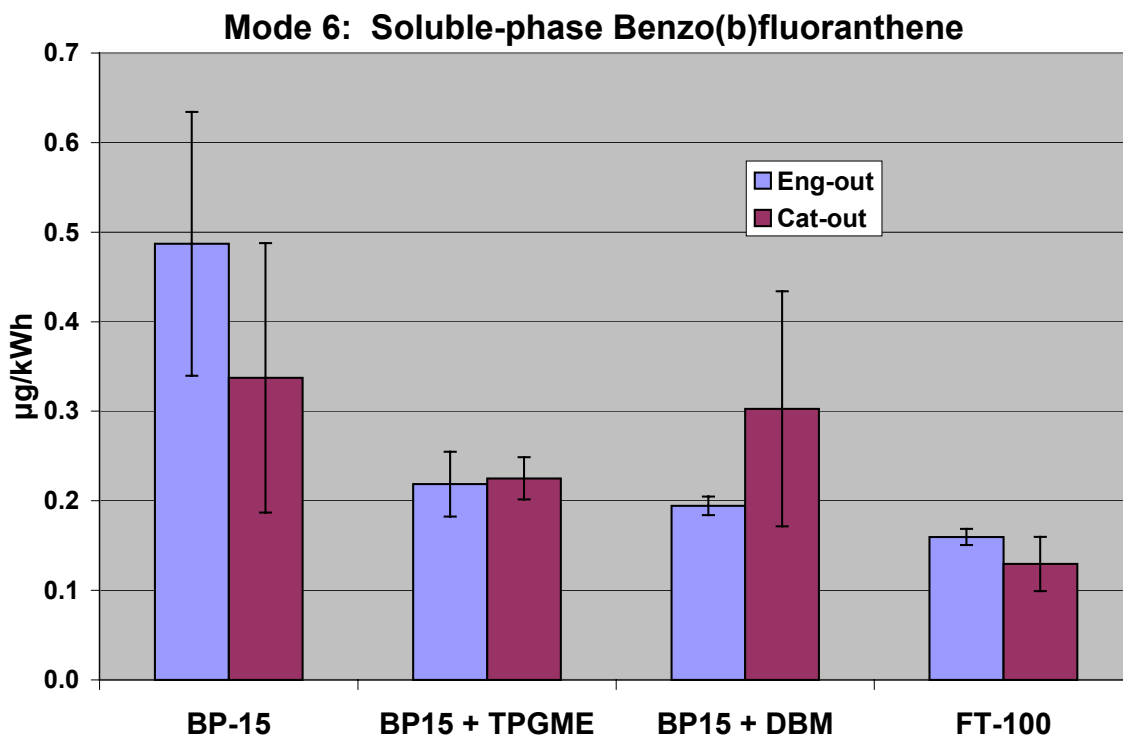


Figure B-35. Soluble-Phase Benzo(b)fluoranthene Emissions by Fuel Type, Mode 6

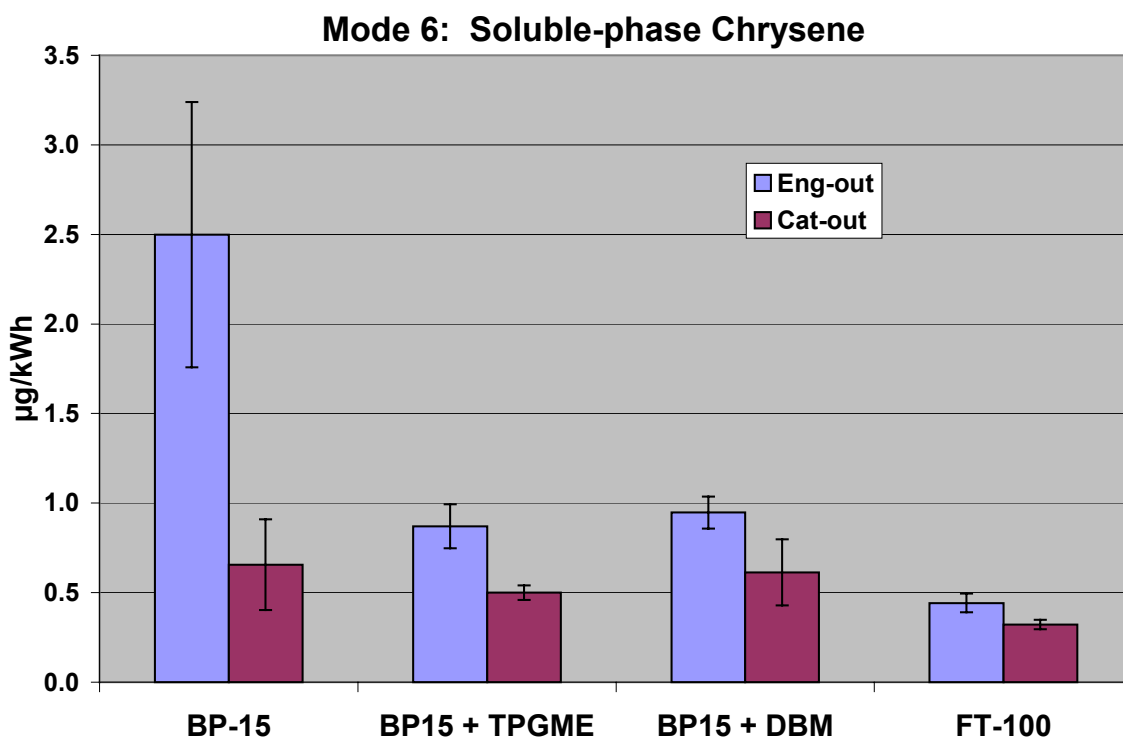


Figure B-36. Soluble-Phase Chrysene Emissions by Fuel Type, Mode 6

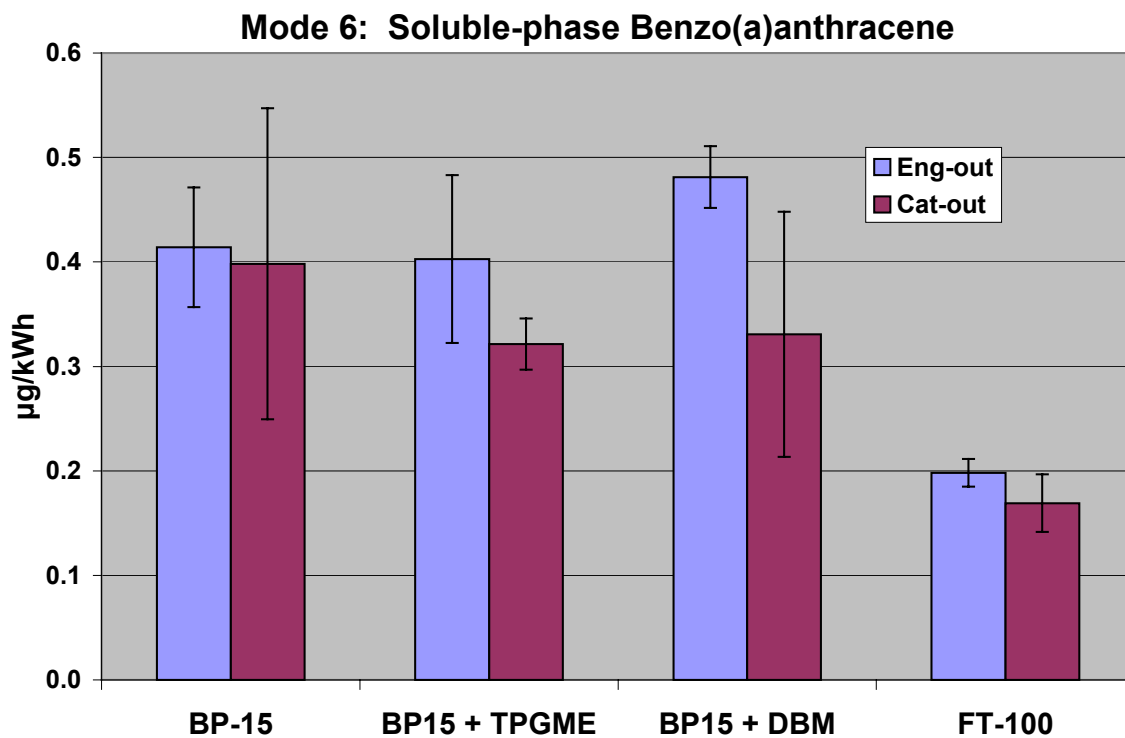


Figure B-37. Soluble-Phase Benzo(a)anthracene Emissions by Fuel Type, Mode 6

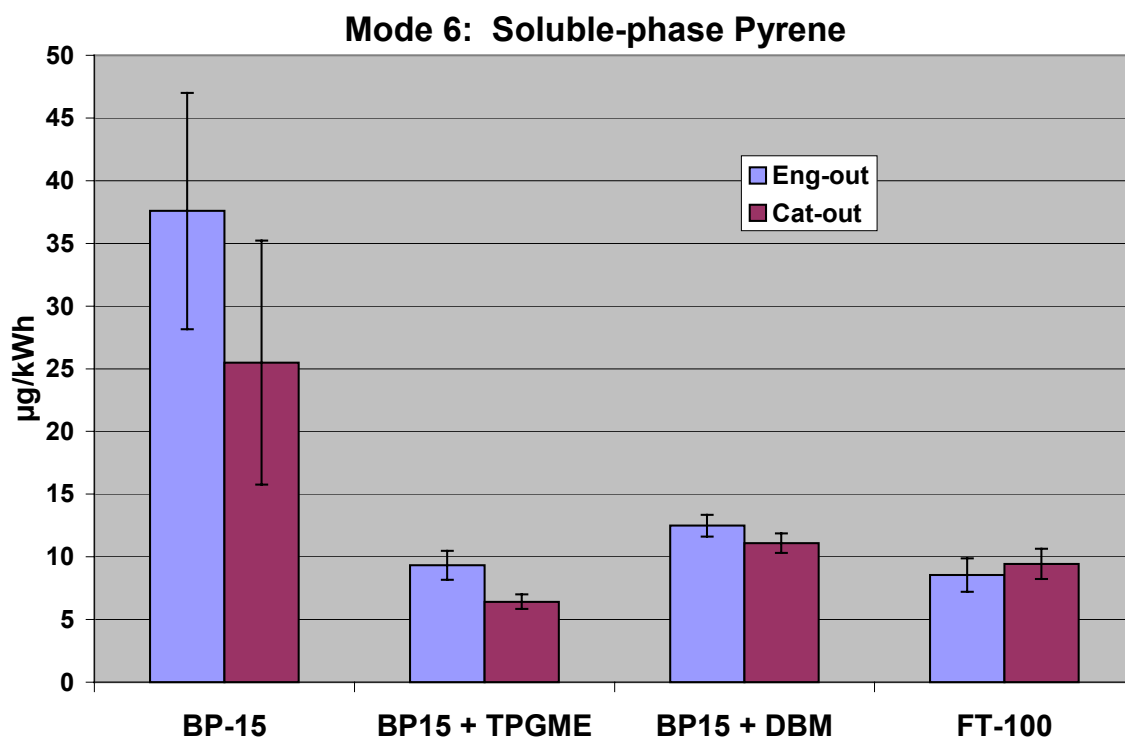


Figure B-38. Soluble-Phase Pyrene Emissions by Fuel Type, Mode 6

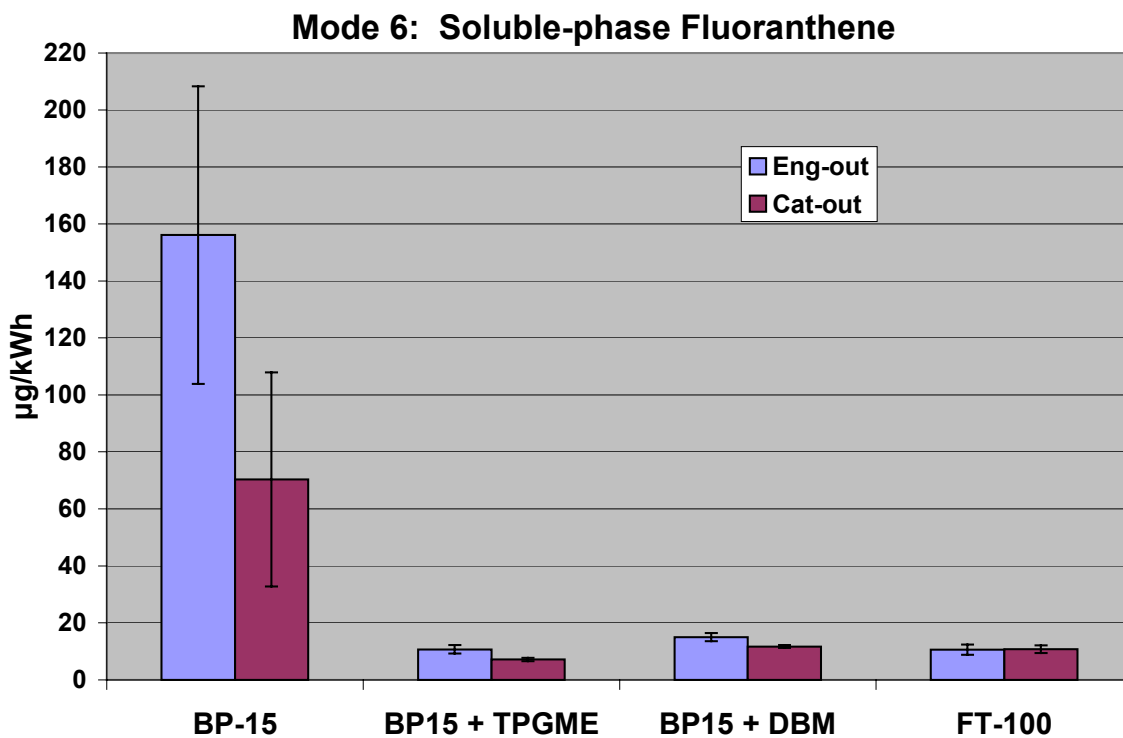


Figure B-39. Soluble-Phase Fluoranthene Emissions by Fuel Type, Mode 6

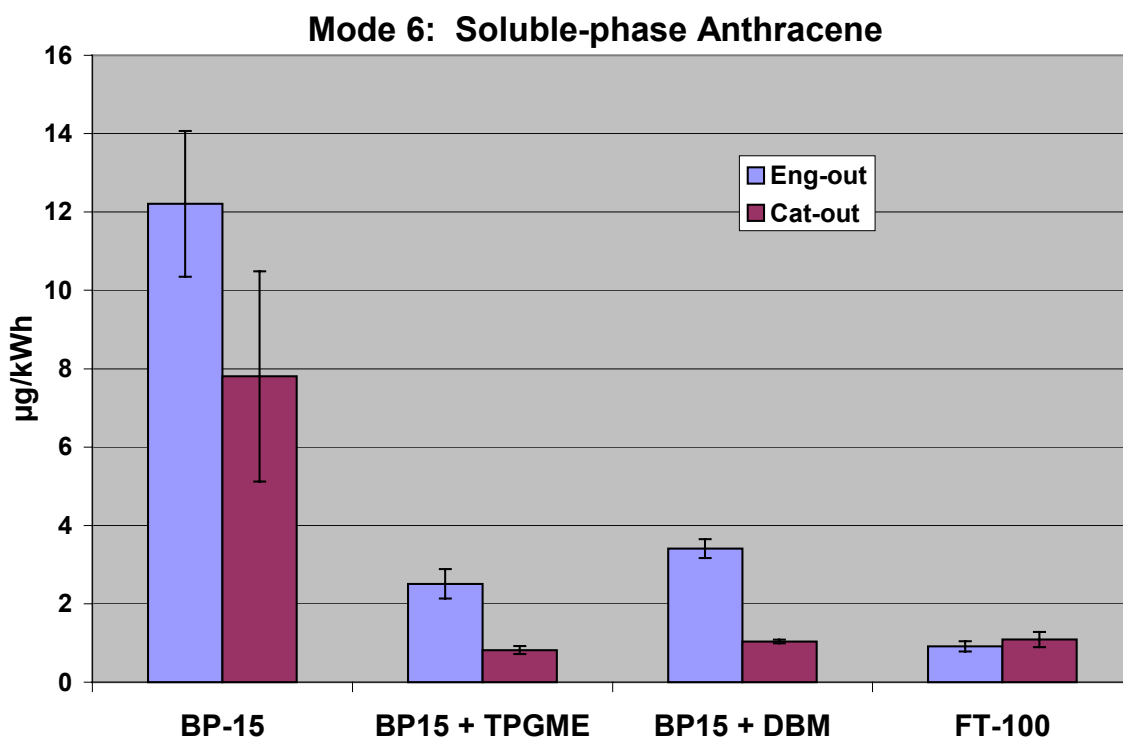


Figure B-40. Soluble-Phase Anthracene Emissions by Fuel Type, Mode 6

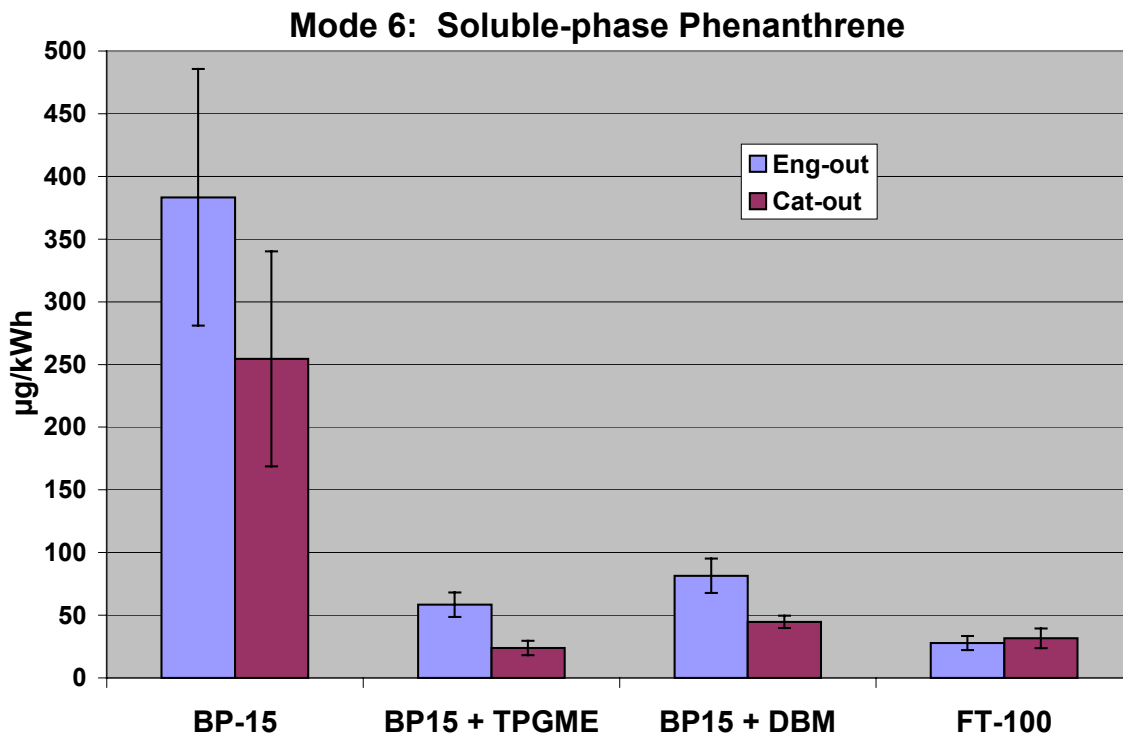


Figure B-41. Soluble-Phase Phenanthrene Emissions by Fuel Type, Mode 6

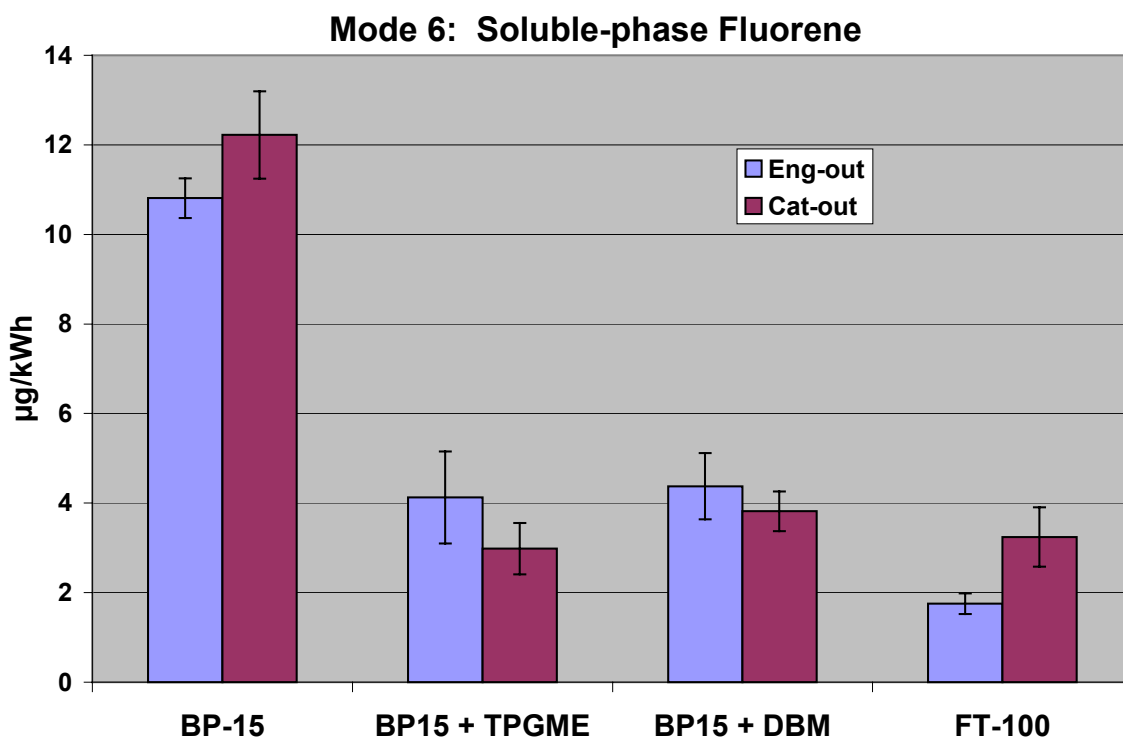


Figure B-42. Soluble-Phase Fluorene Emissions by Fuel Type, Mode 6

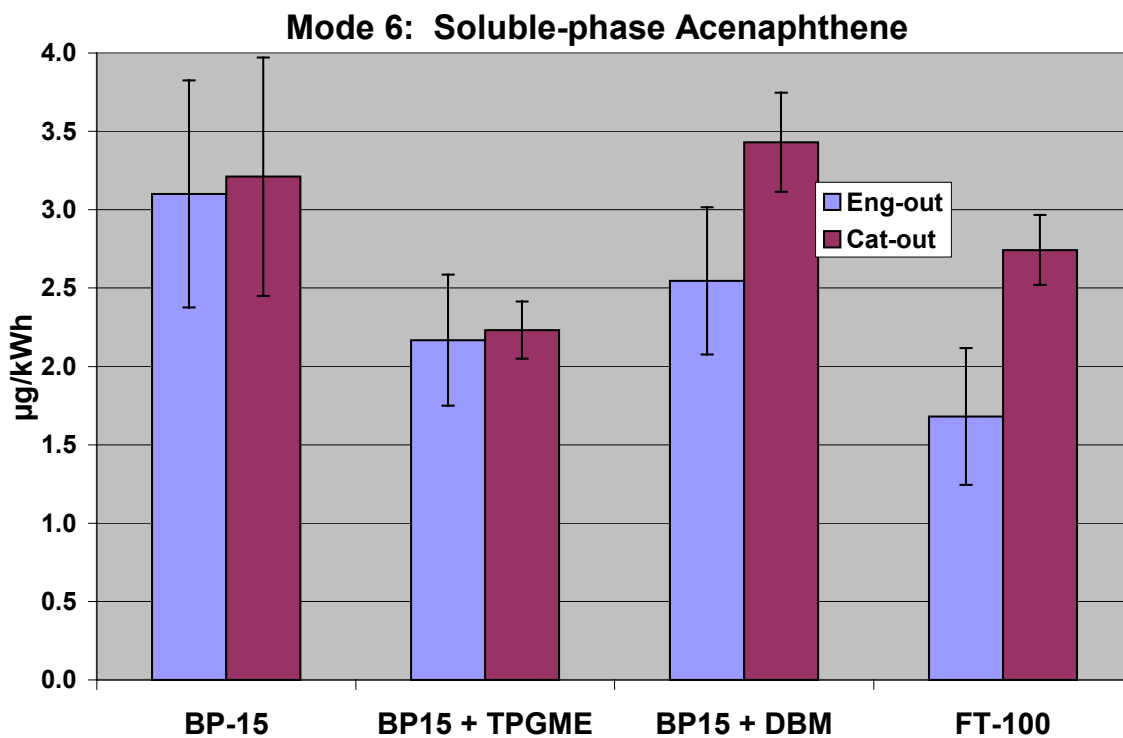


Figure B-43. Soluble-Phase Acenaphthene Emissions by Fuel Type, Mode 6

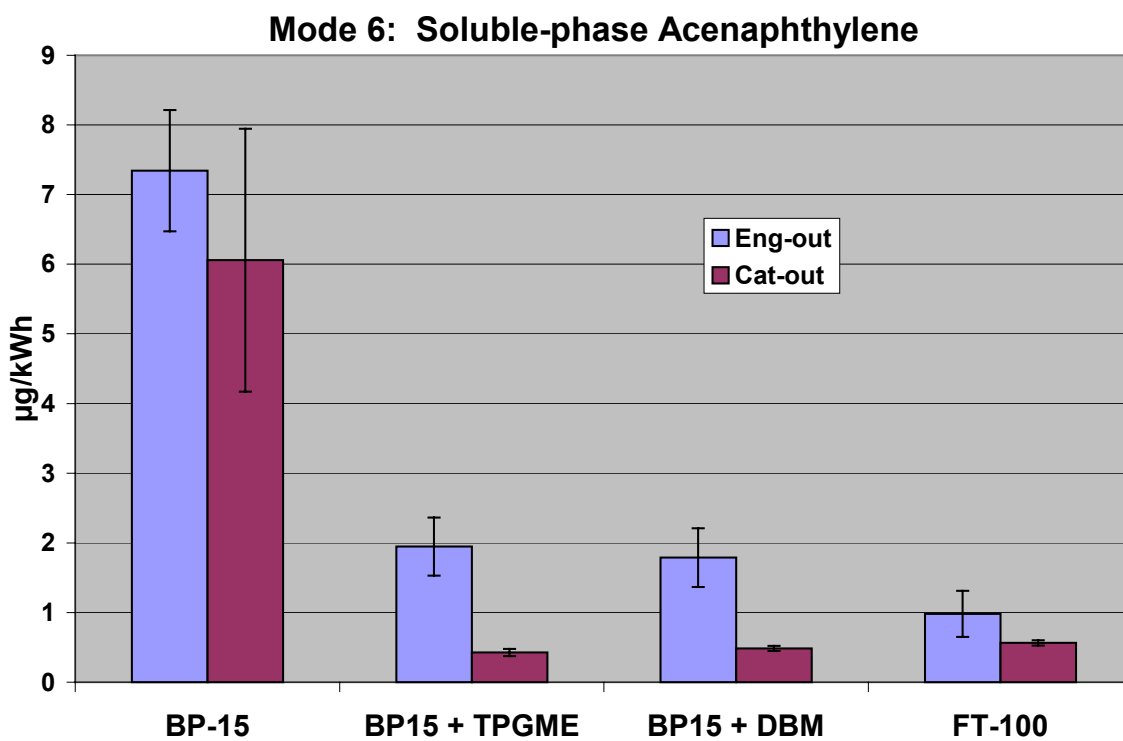


Figure B-44. Soluble-Phase Acenaphthylene Emissions by Fuel Type, Mode 6

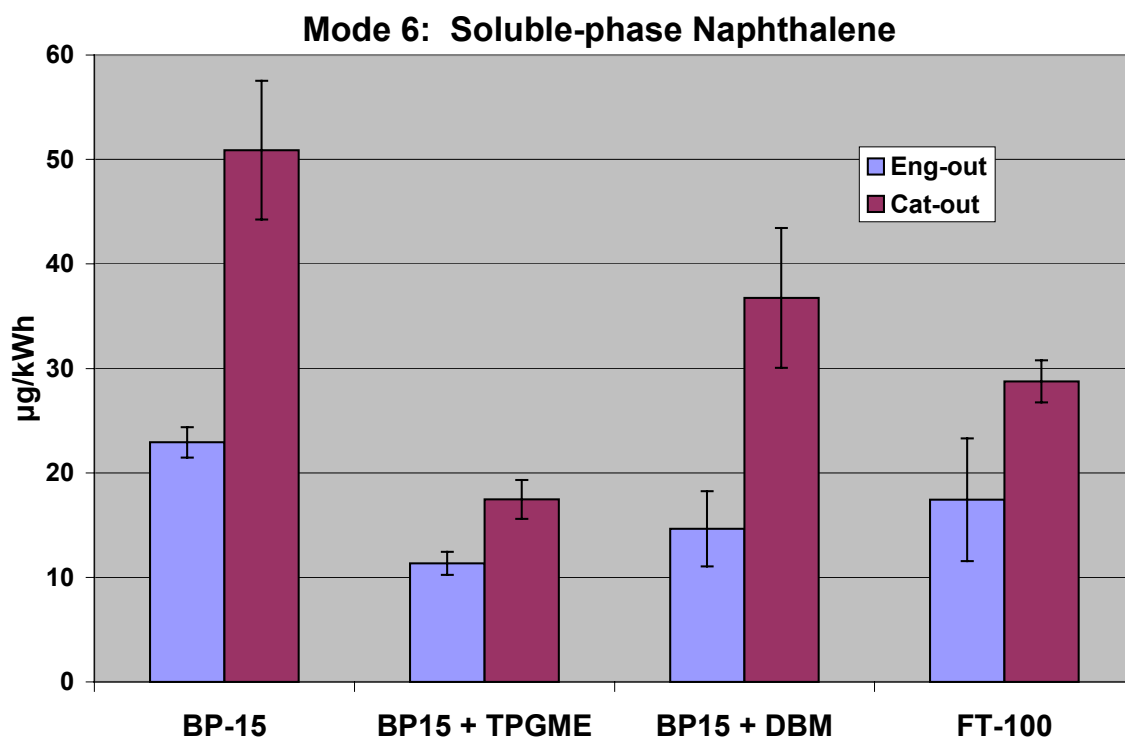


Figure B-45. Soluble-Phase Naphthalene Emissions by Fuel Type, Mode 6

## **APPENDIX C**

### **Mode 11 Operation Test Results**



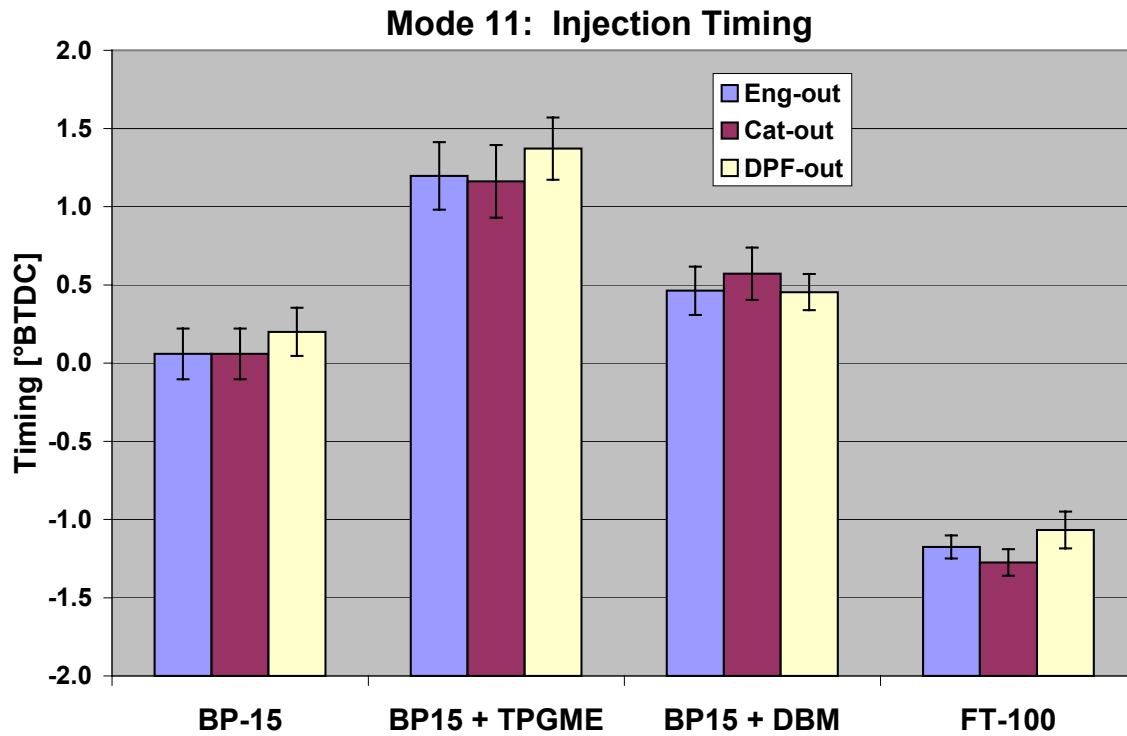


Figure C-1. Injection Timing by Fuel Type, Mode 11

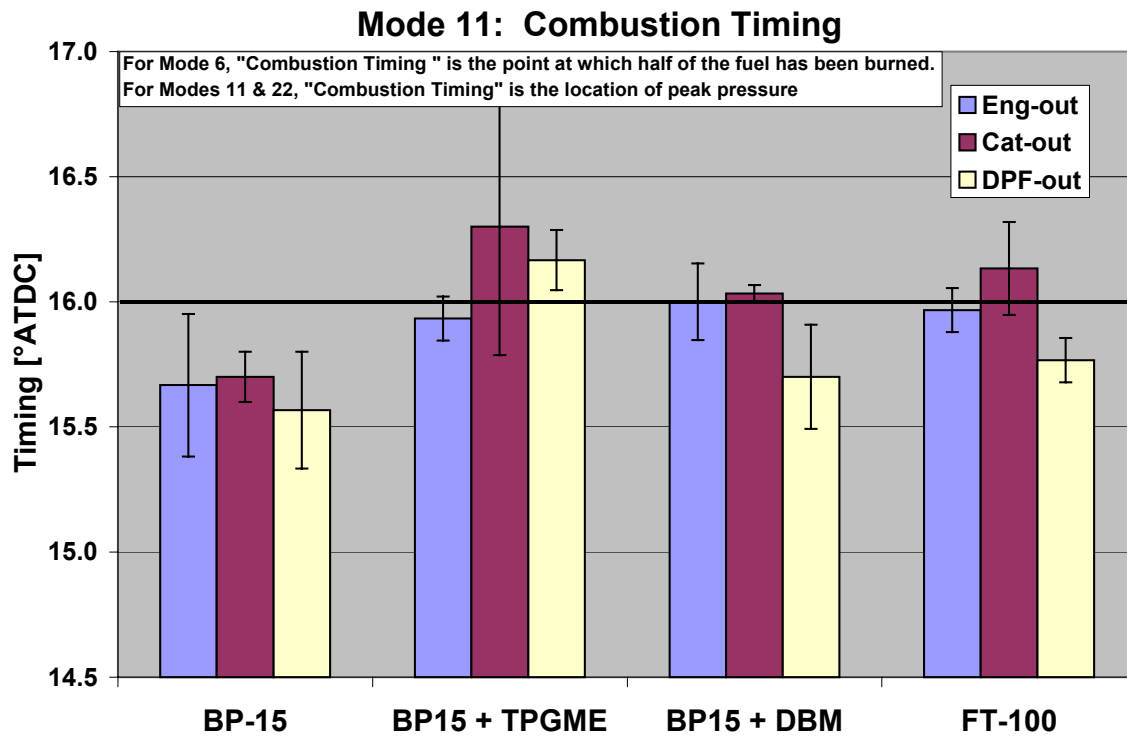


Figure C-2. Combustion Timing by Fuel Type, Mode 11

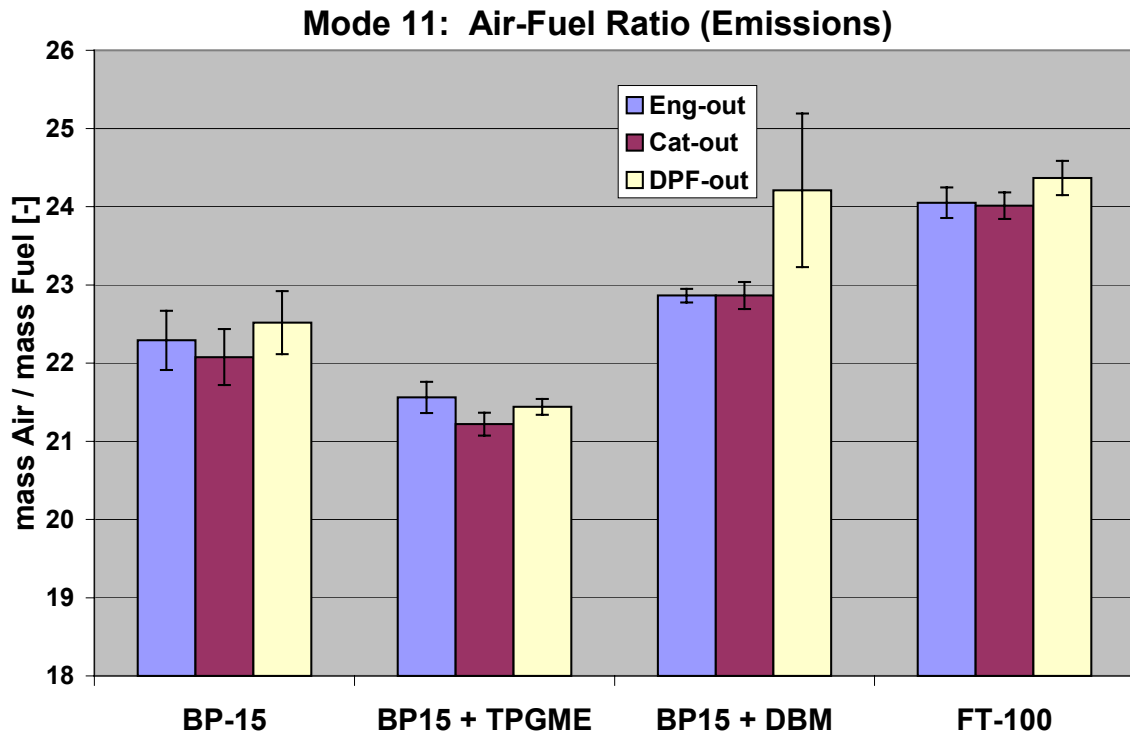


Figure C-3. Emissions Air-Fuel Ratio by Fuel Type, Mode 11

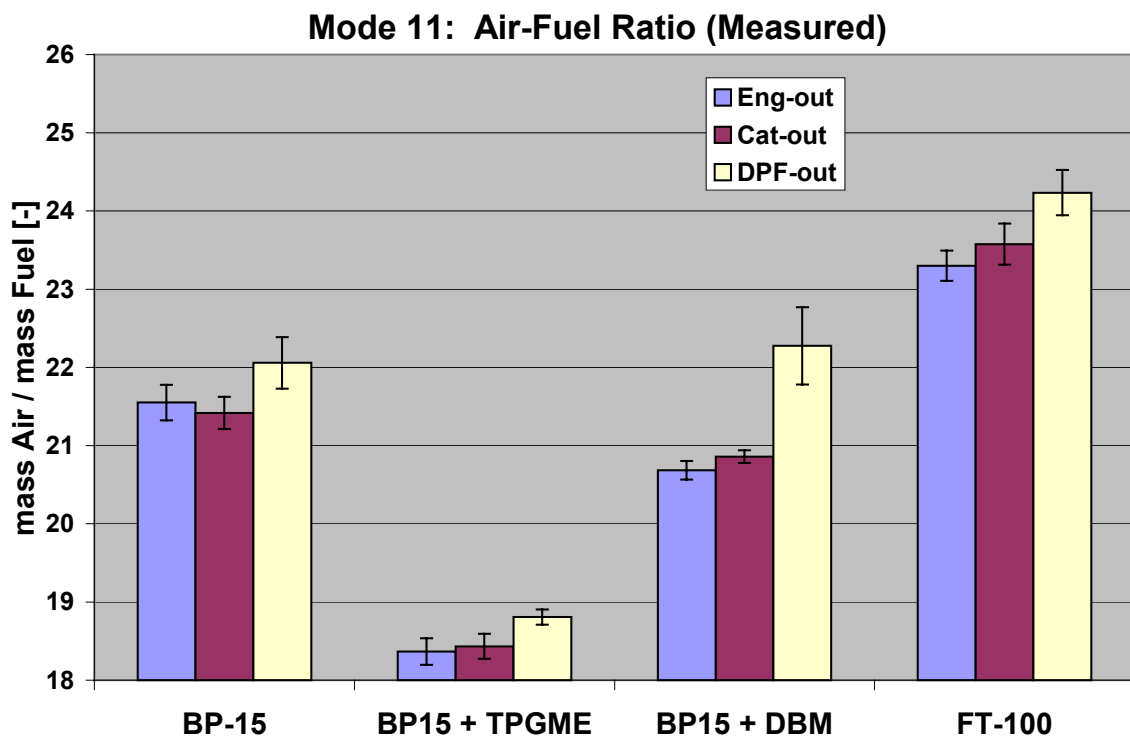


Figure C-4. Measured Air-Fuel Ratio by Fuel Type, Mode 11

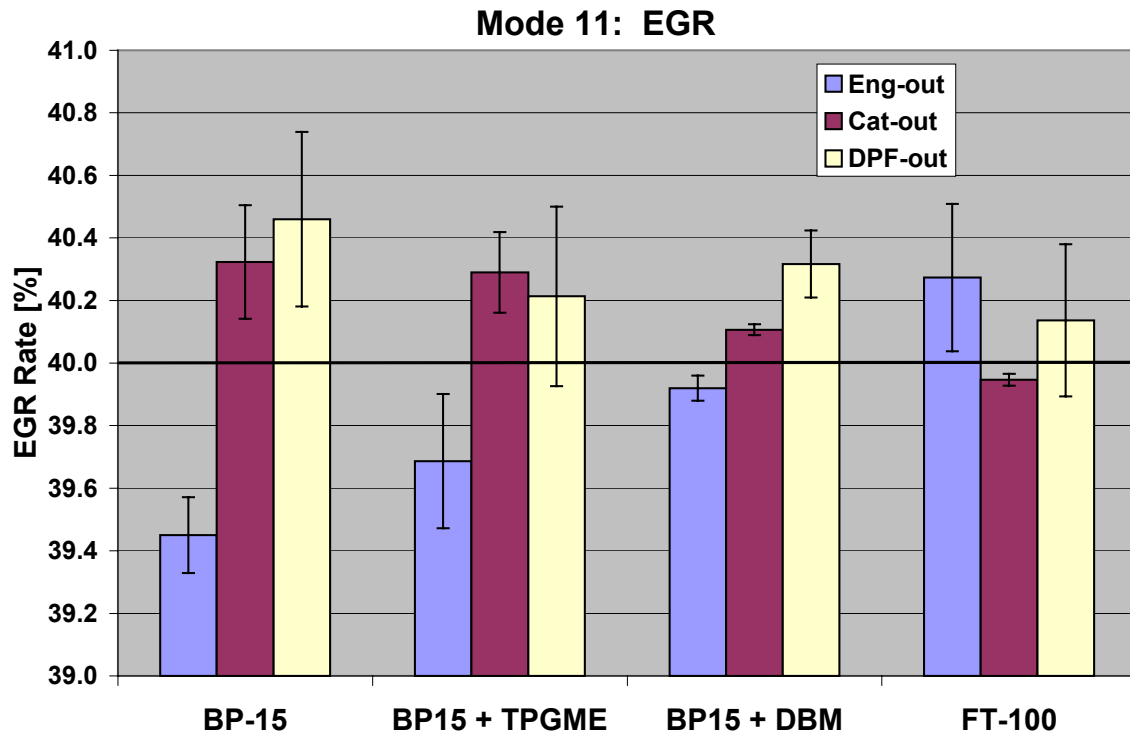


Figure C-5. EGR Rate by Fuel Type, Mode 11

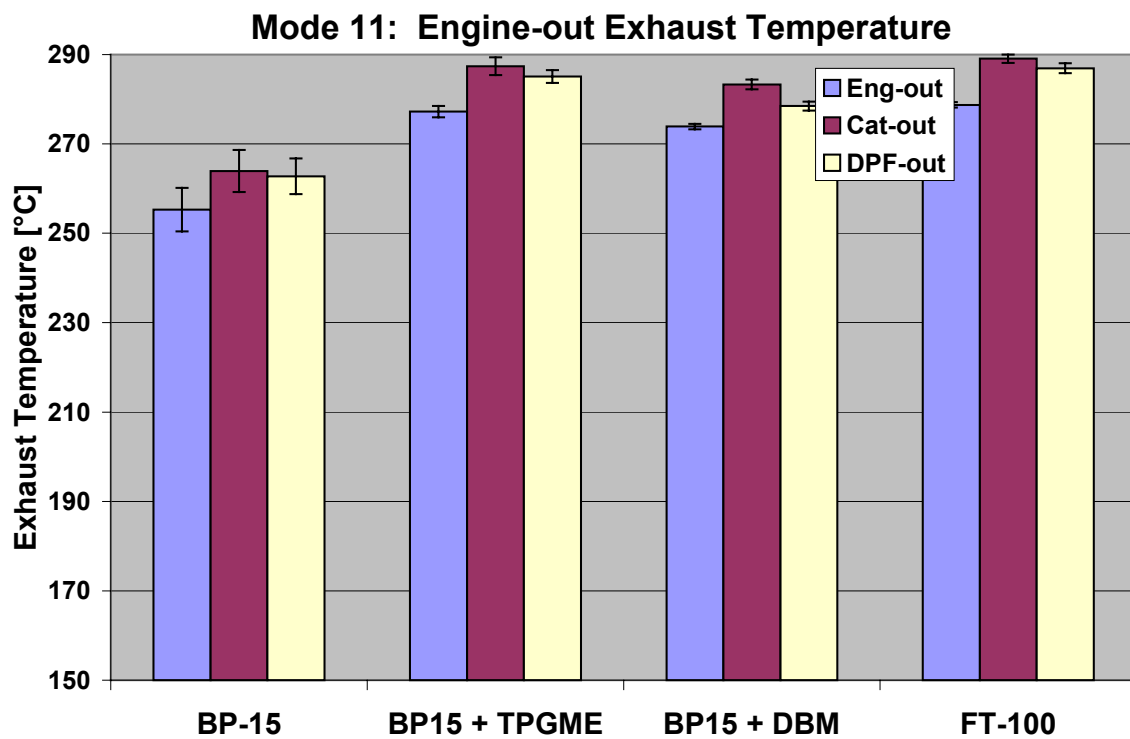


Figure C-6. Engine-Out Exhaust Temperature by Fuel Type, Mode 11

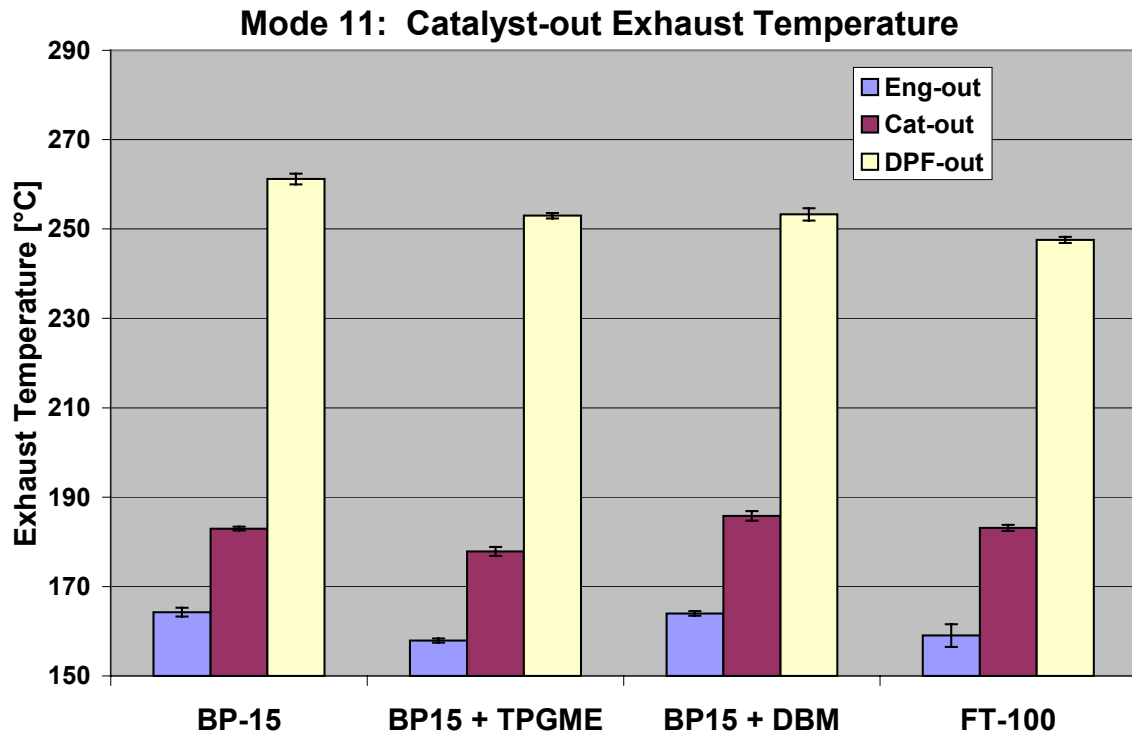


Figure C-7. Catalyst-Out Exhaust Temperature by Fuel Type, Mode 11

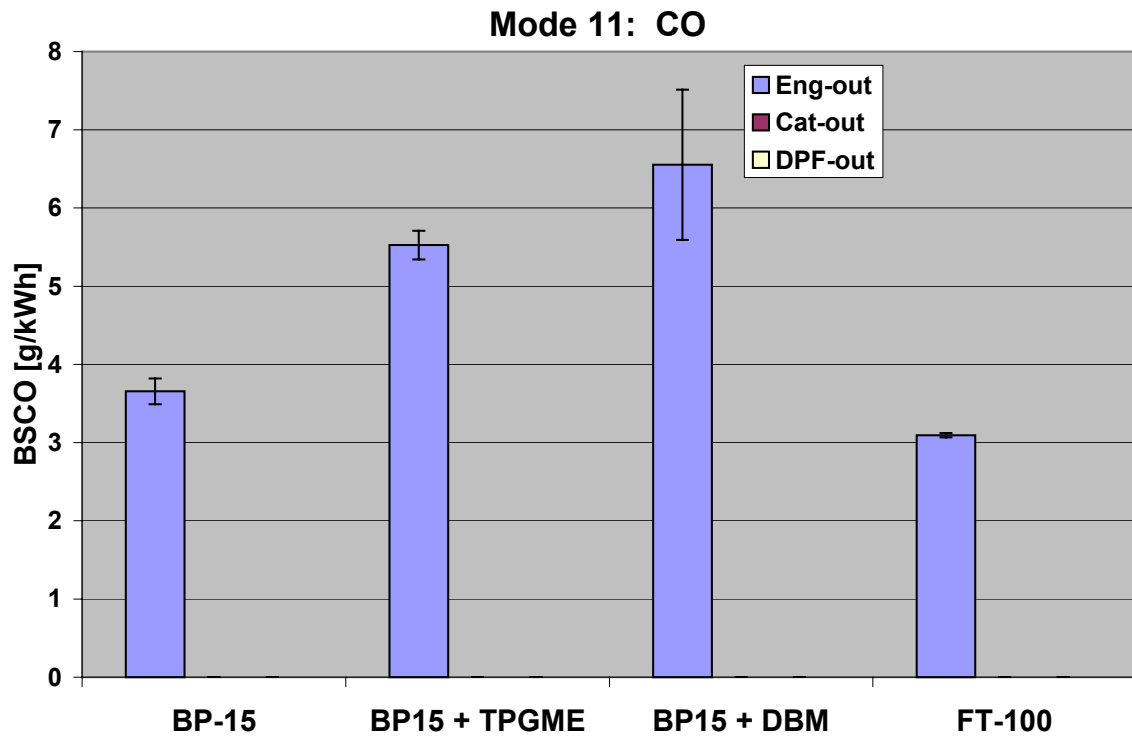


Figure C-8. Carbon Monoxide Emissions by Fuel Type, Mode 11

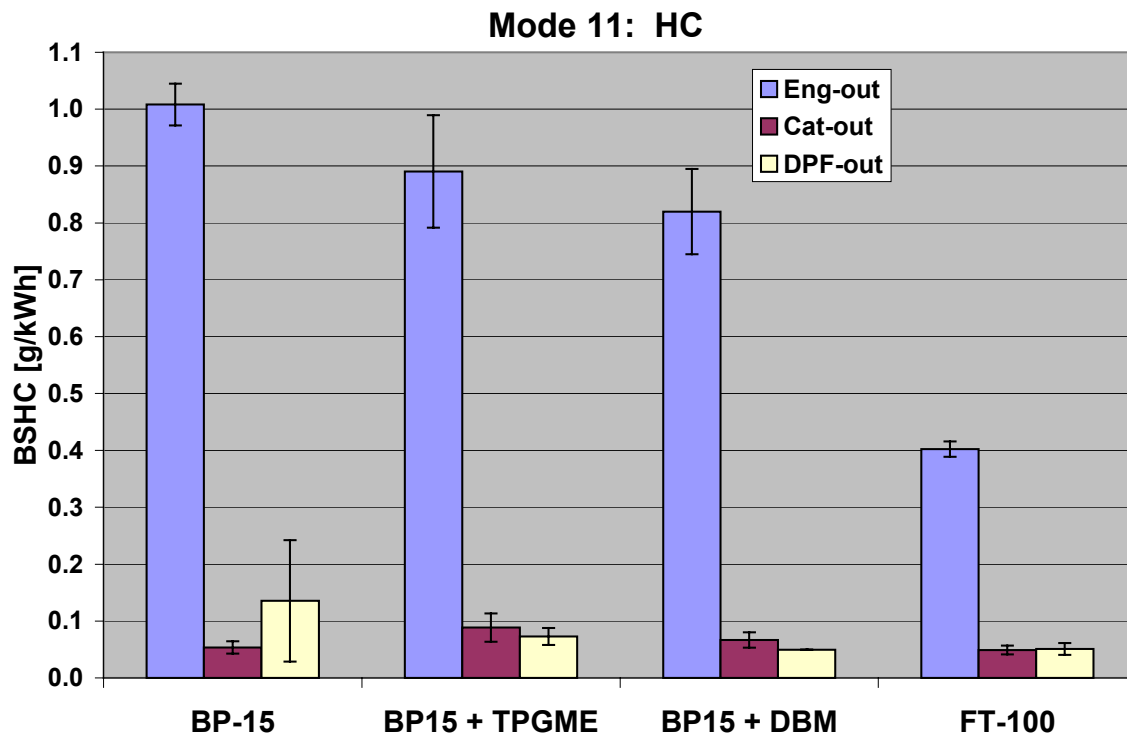


Figure C-9. Hydrocarbon Emissions by Fuel Type, Mode 11

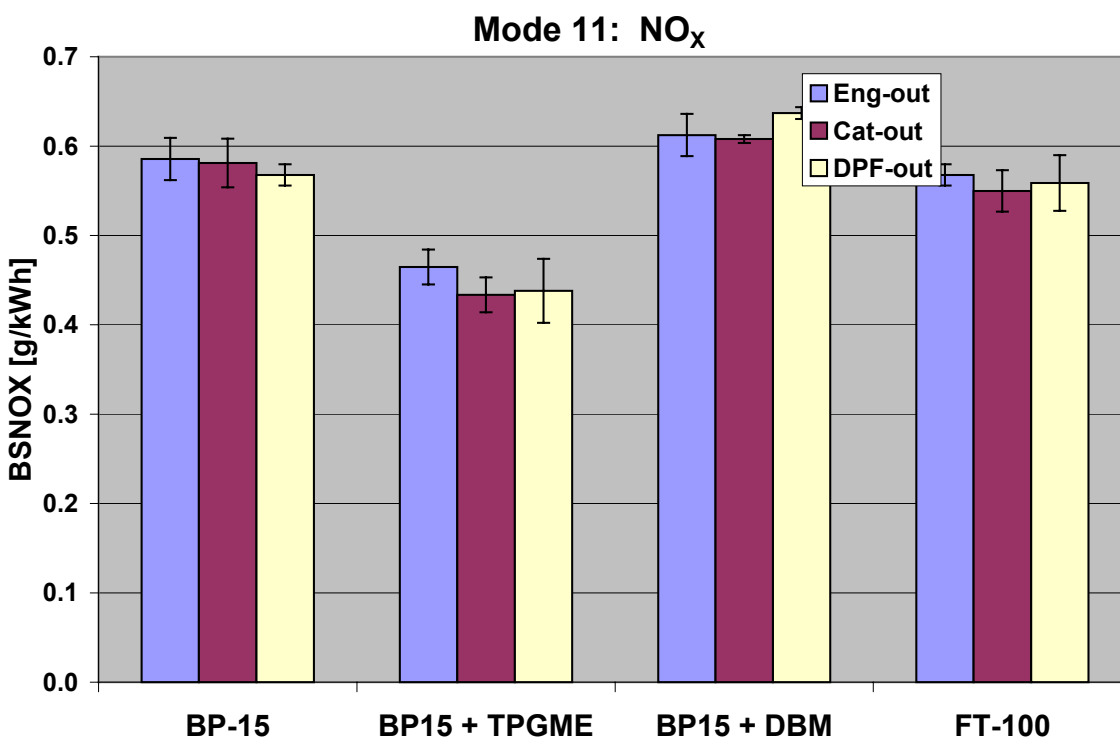


Figure C-10. Nitrogen Oxides Emissions by Fuel Type, Mode 11

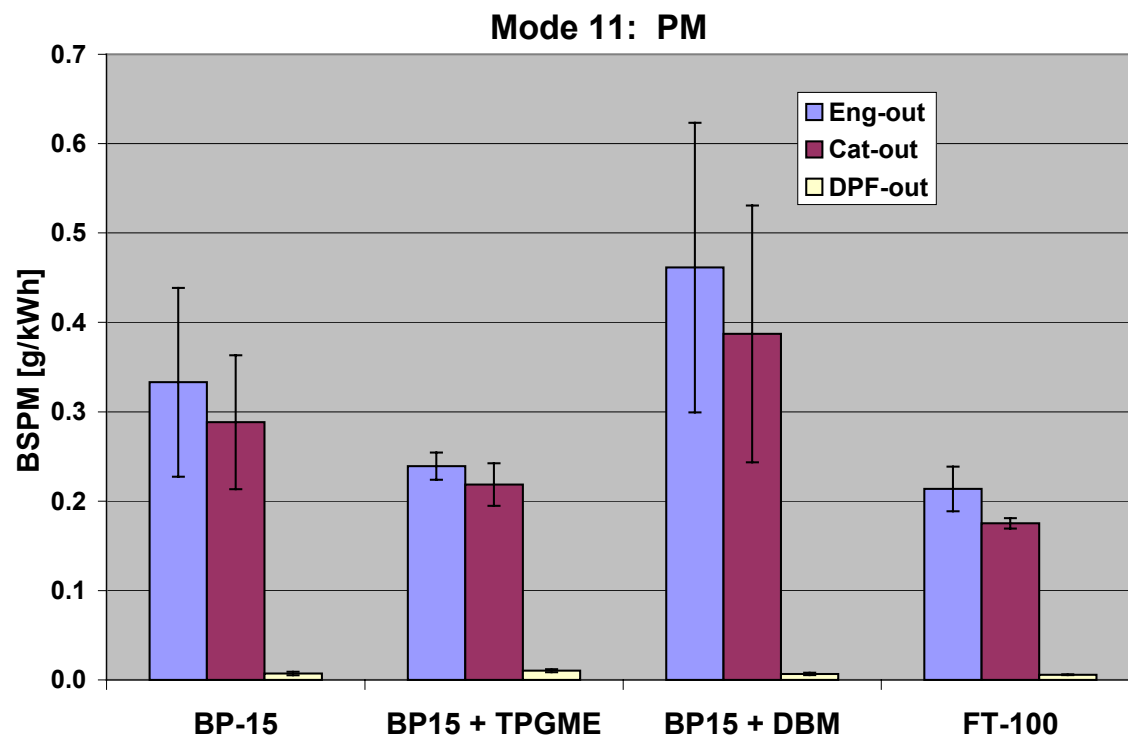


Figure C-11. Particulate Matter Emissions by Fuel Type, Mode 11

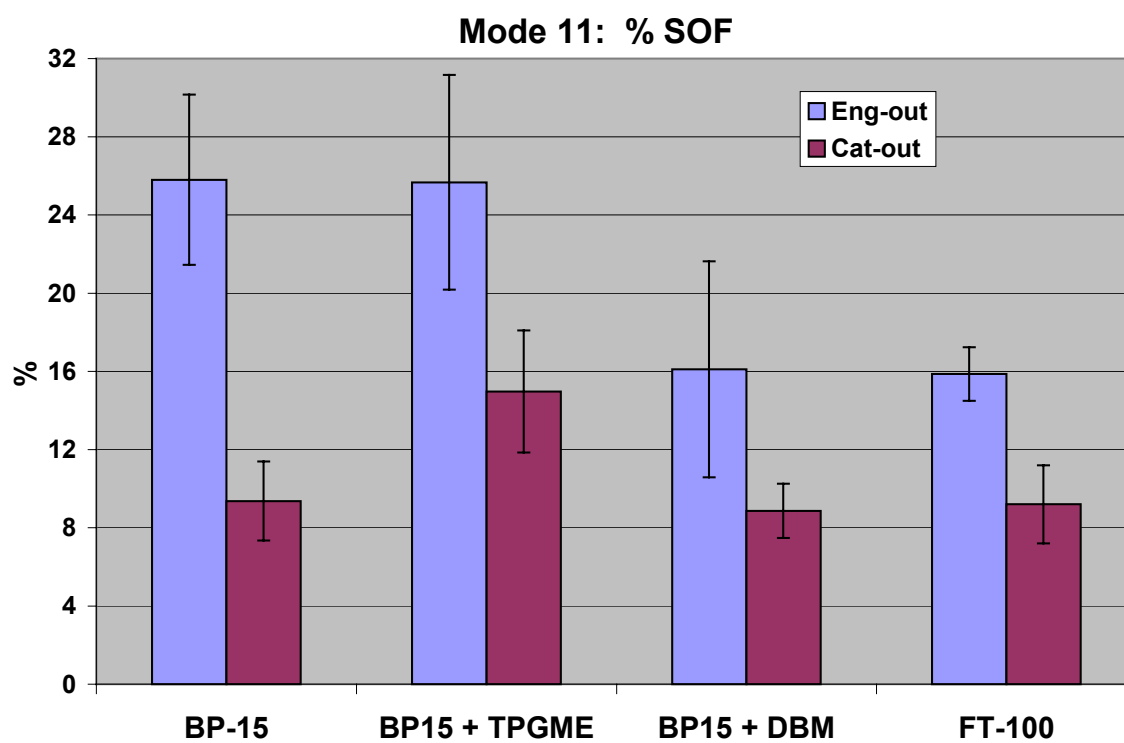


Figure C-12. Percent Soluble Organic Fraction by Fuel Type, Mode 11

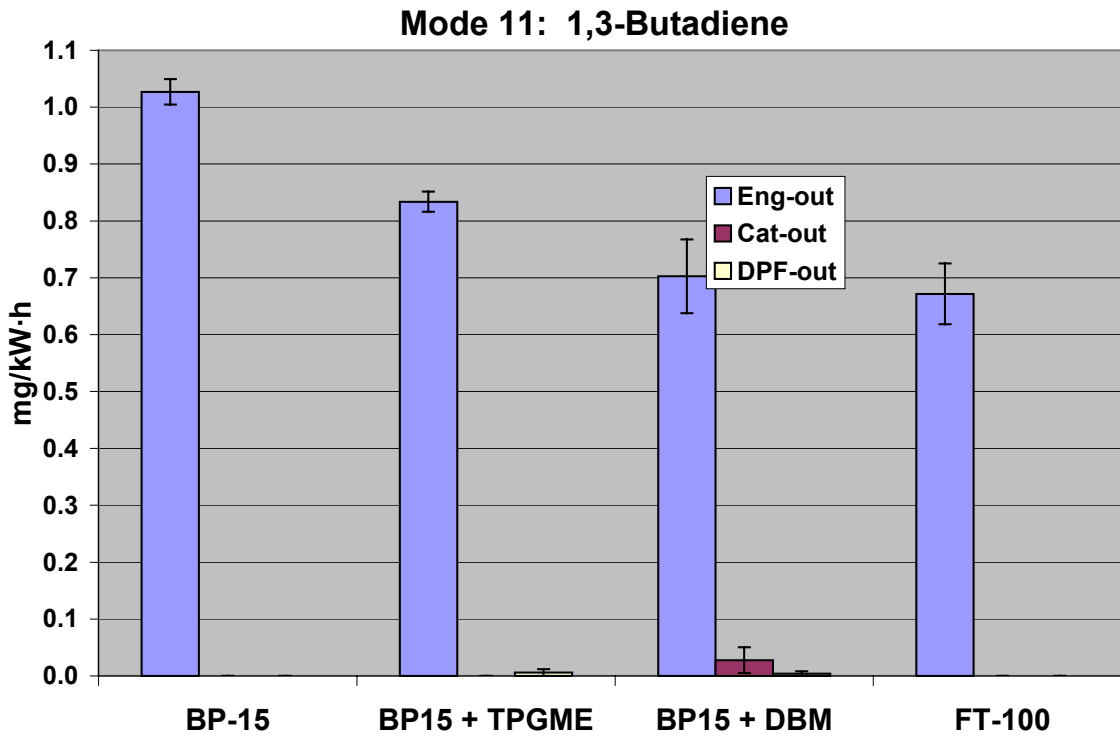


Figure C-13. 1,3-Butadiene Emissions by Fuel Type, Mode 11

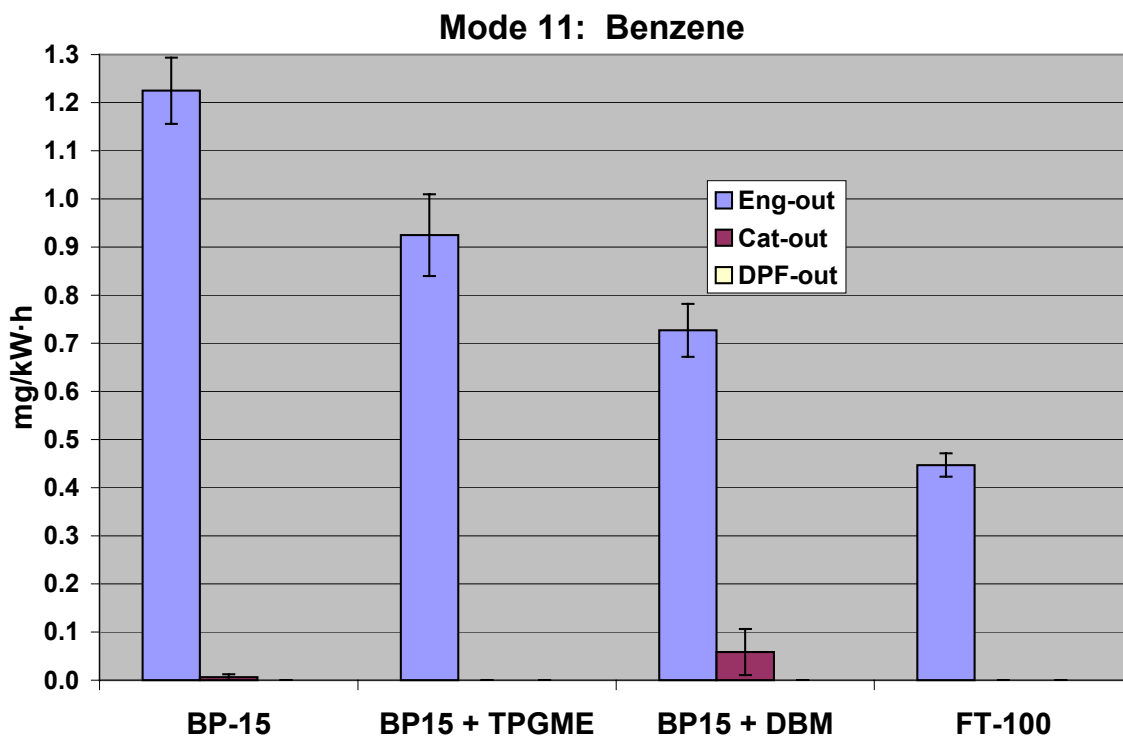


Figure C-14. Benzene Emissions by Fuel Type, Mode 11

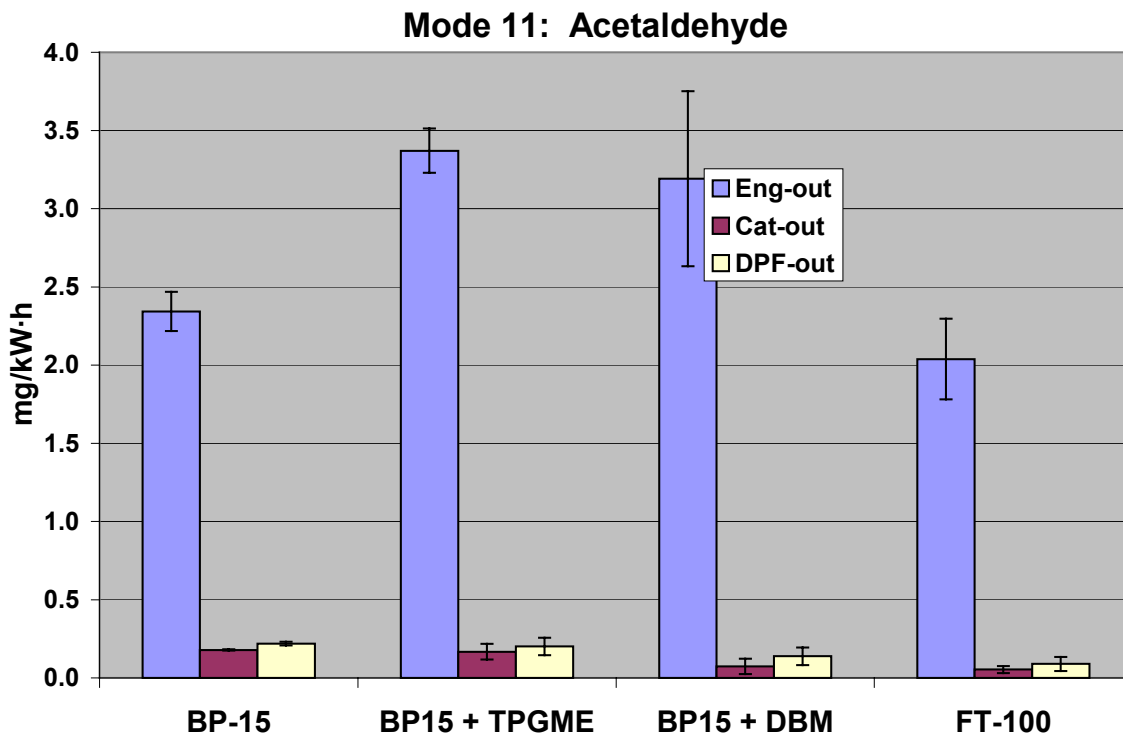


Figure C-15. Acetaldehyde Emissions by Fuel Type, Mode 11

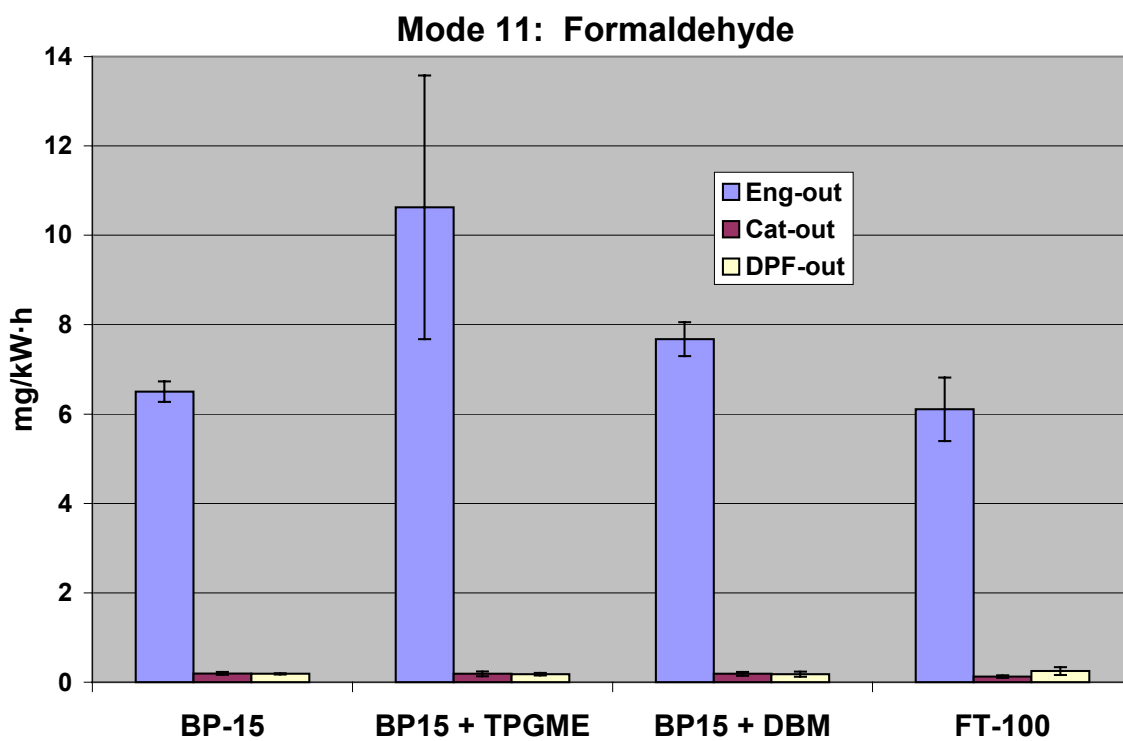


Figure C-16. Formaldehyde Emissions by Fuel Type, Mode 11



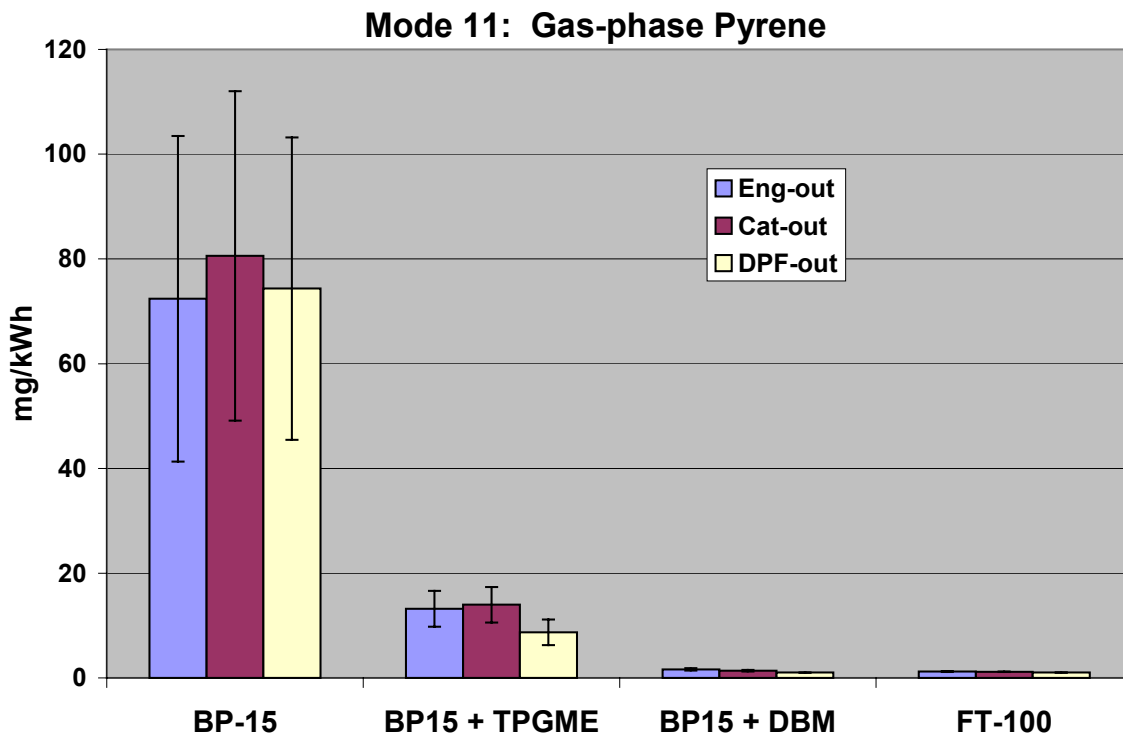


Figure C-17. Gas-Phase Pyrene Emissions by Fuel Type, Mode 11

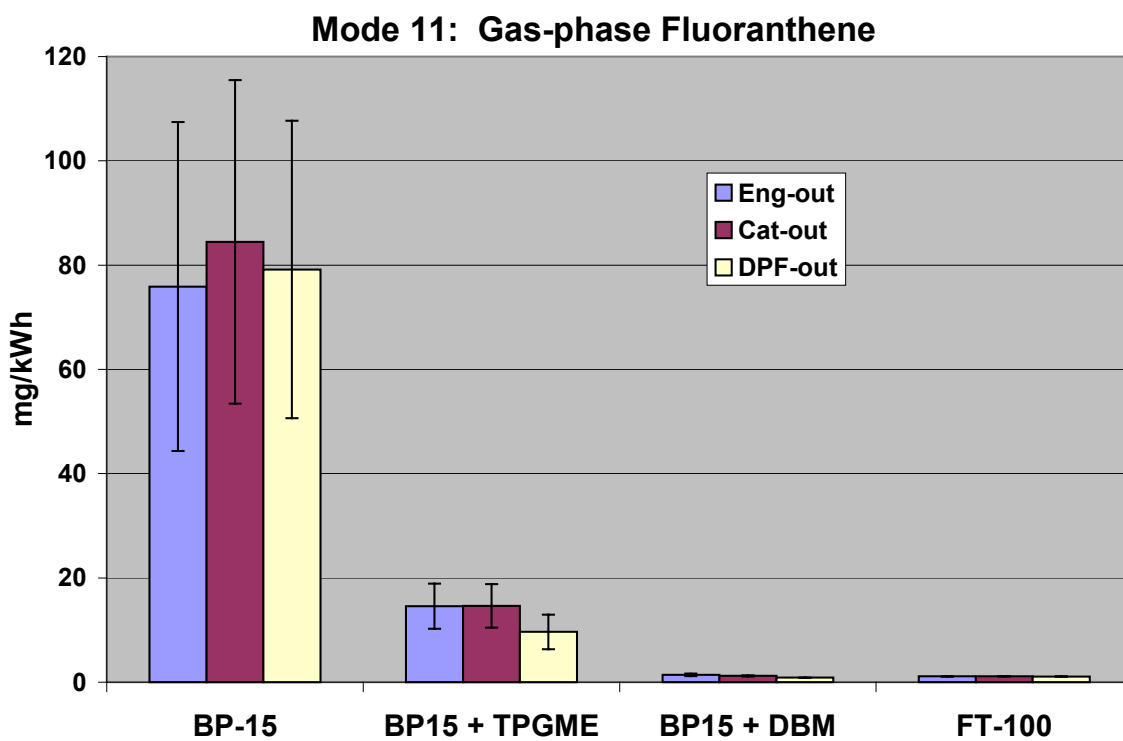


Figure C-18. Gas-Phase Fluoranthene Emissions by Fuel Type, Mode 11

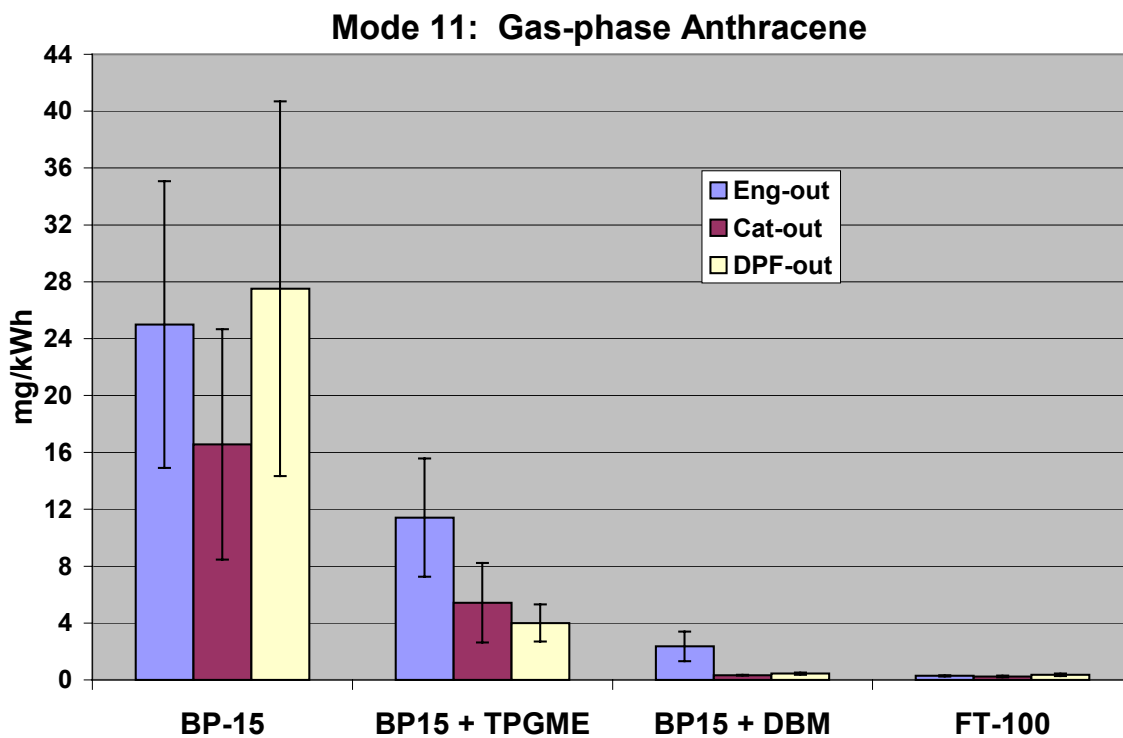


Figure C-19. Gas-Phase Anthracene Emissions by Fuel Type, Mode 11

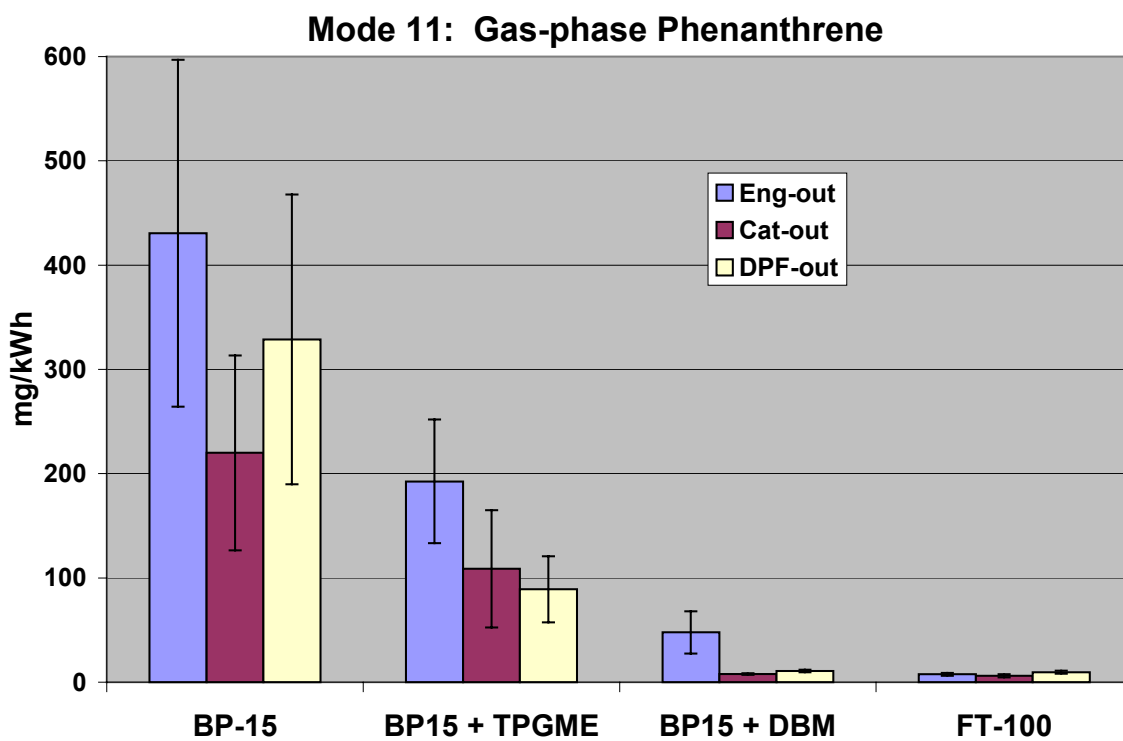


Figure C-20. Gas-Phase Phenanthrene Emissions by Fuel Type, Mode 11

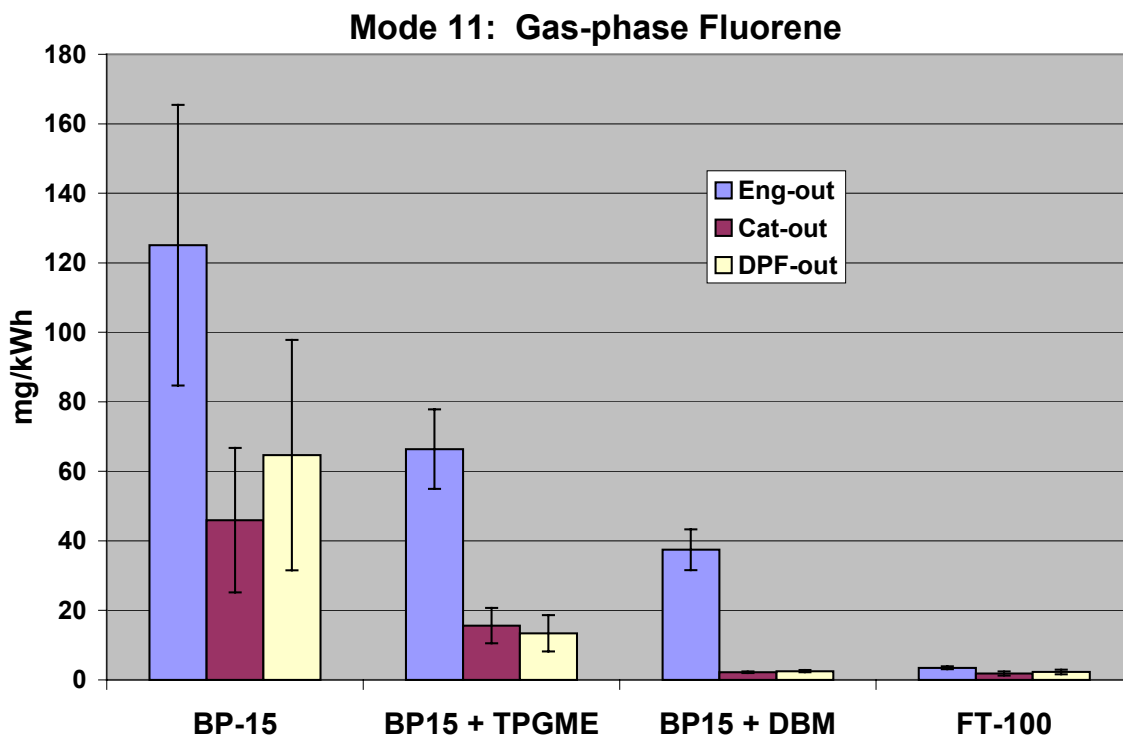


Figure C-21. Gas-Phase Fluorene Emissions by Fuel Type, Mode 11

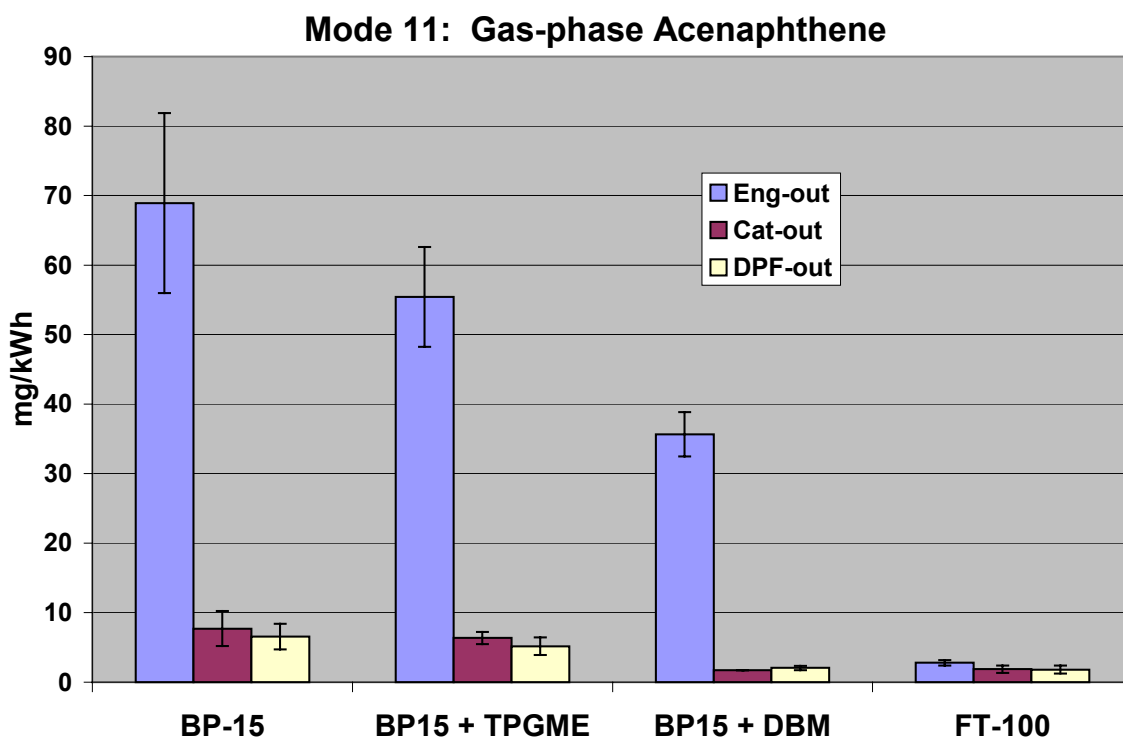


Figure C-22. Gas-Phase Acenaphthene Emissions by Fuel Type, Mode 11

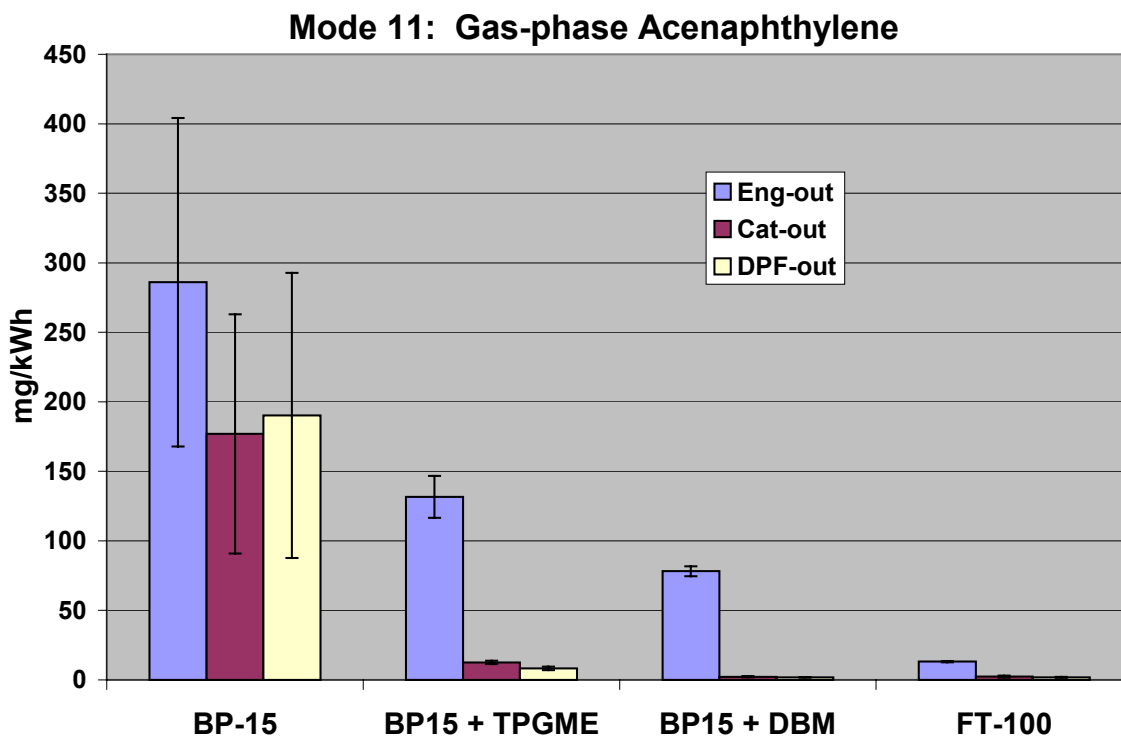


Figure C-23. Gas-Phase Acenaphthylene Emissions by Fuel Type, Mode 11

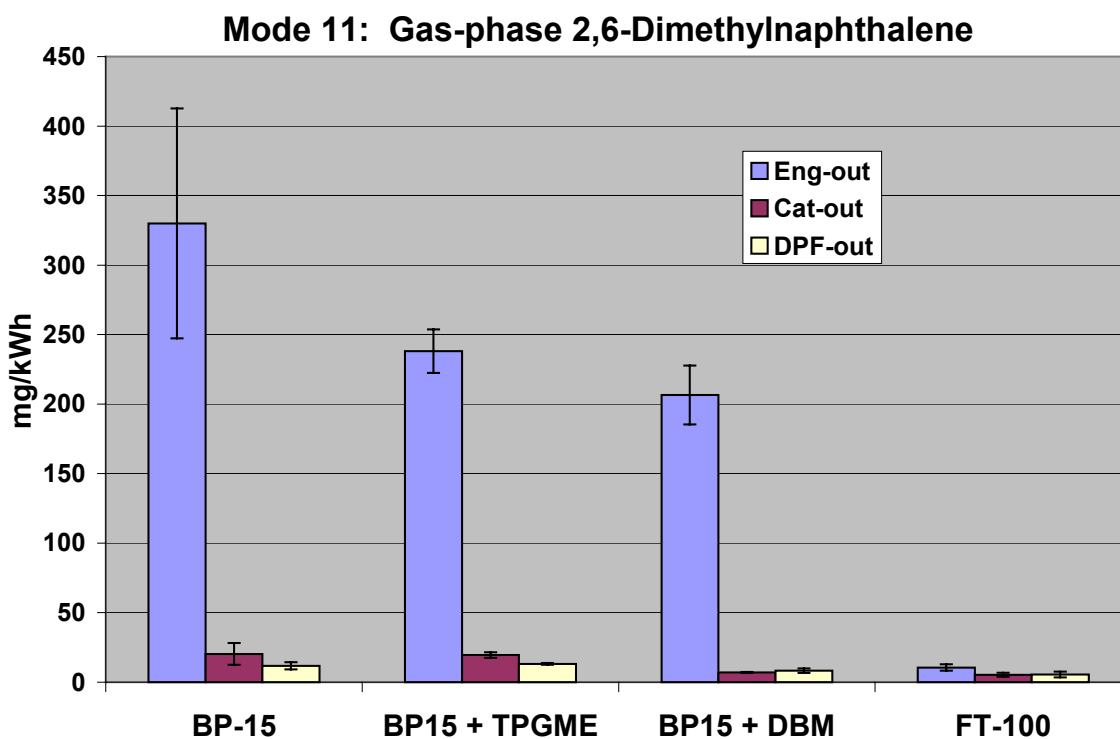


Figure C-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions by Fuel Type, Mode 11

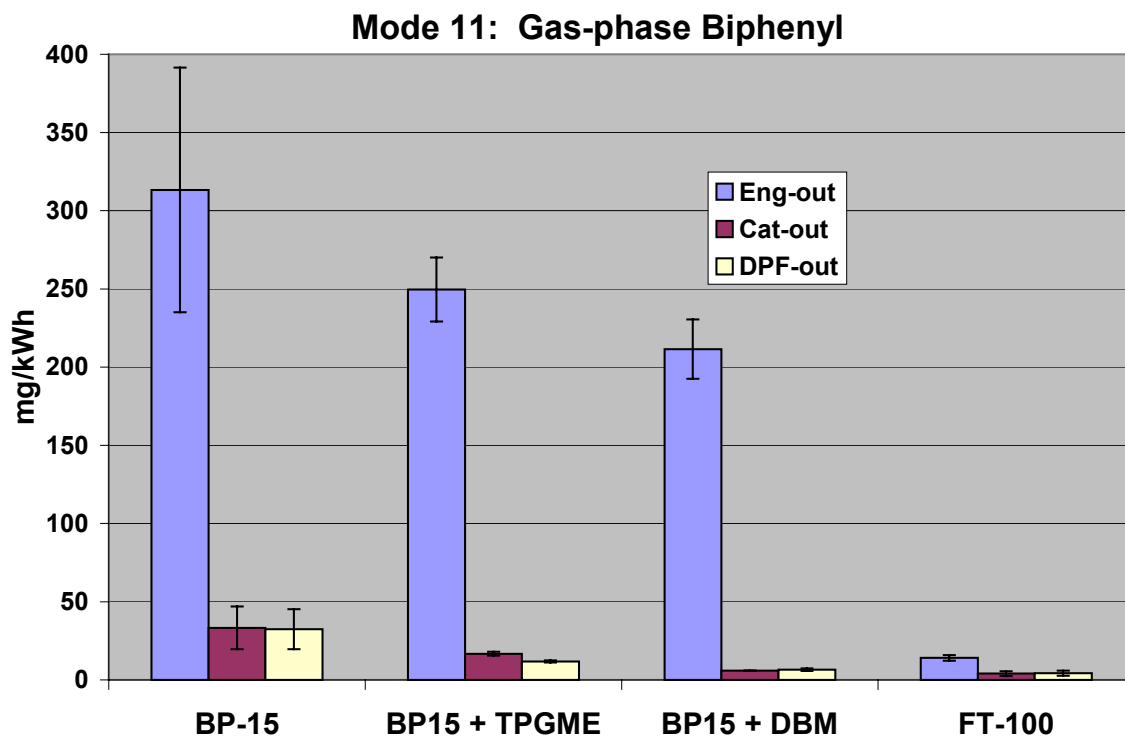


Figure C-25. Gas-Phase Biphenyl Emissions by Fuel Type, Mode 11

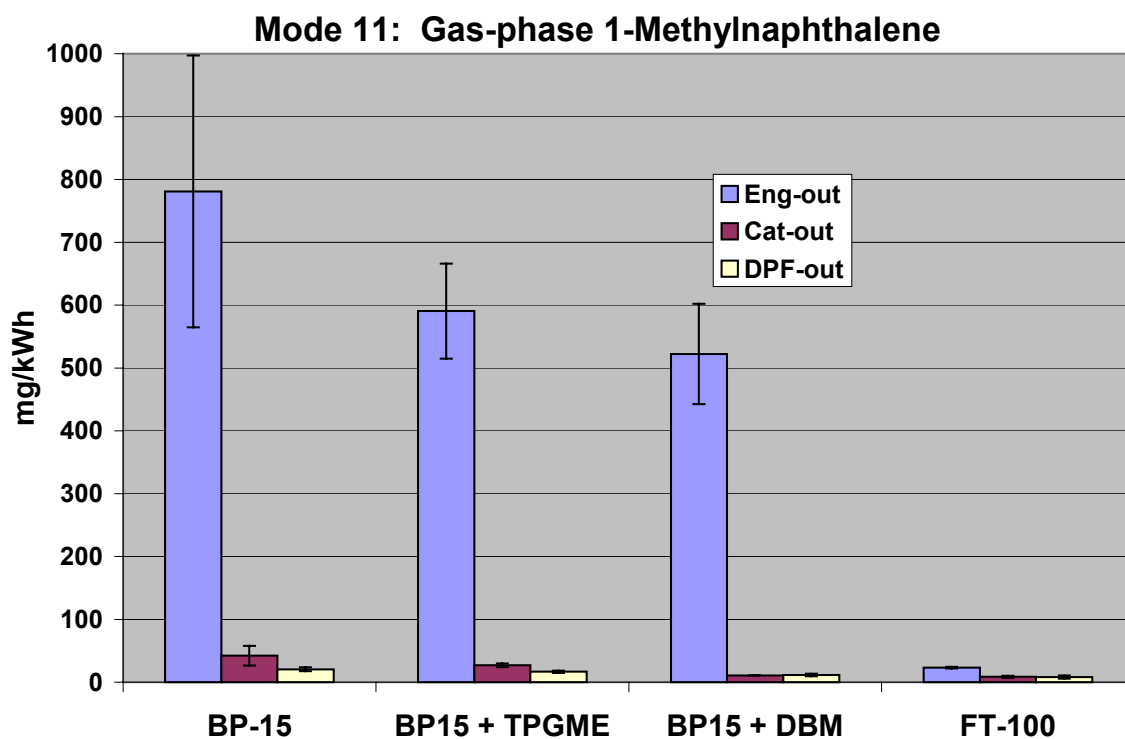


Figure C-26. Gas-Phase 1-Methylnaphthalene Emissions by Fuel Type, Mode 11

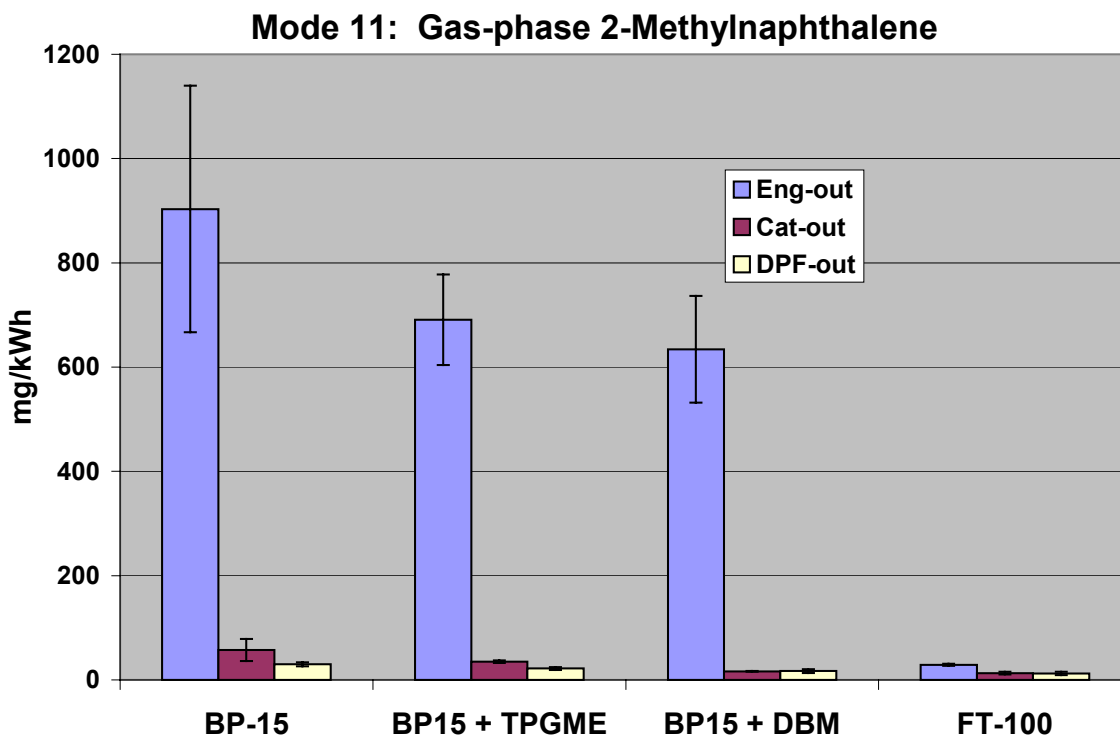


Figure C-27. Gas-Phase 2-Methylnaphthalene Emissions by Fuel Type, Mode 11

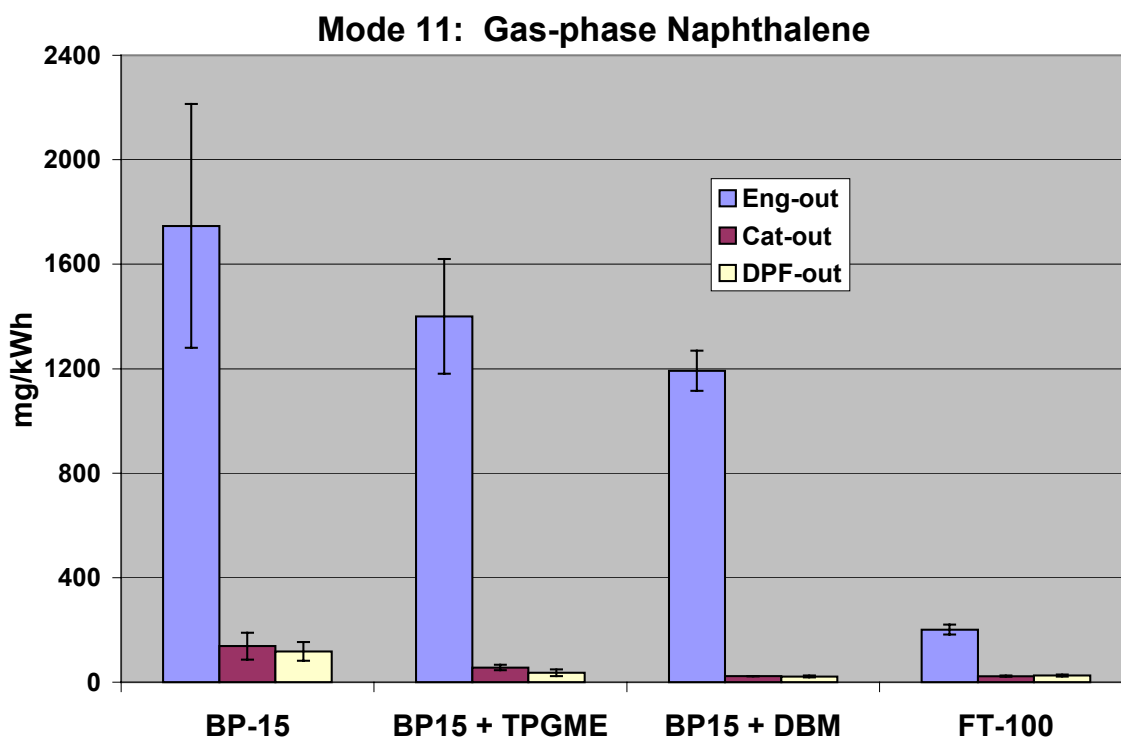


Figure C-28. Gas-Phase Naphthalene Emissions by Fuel Type, Mode 11

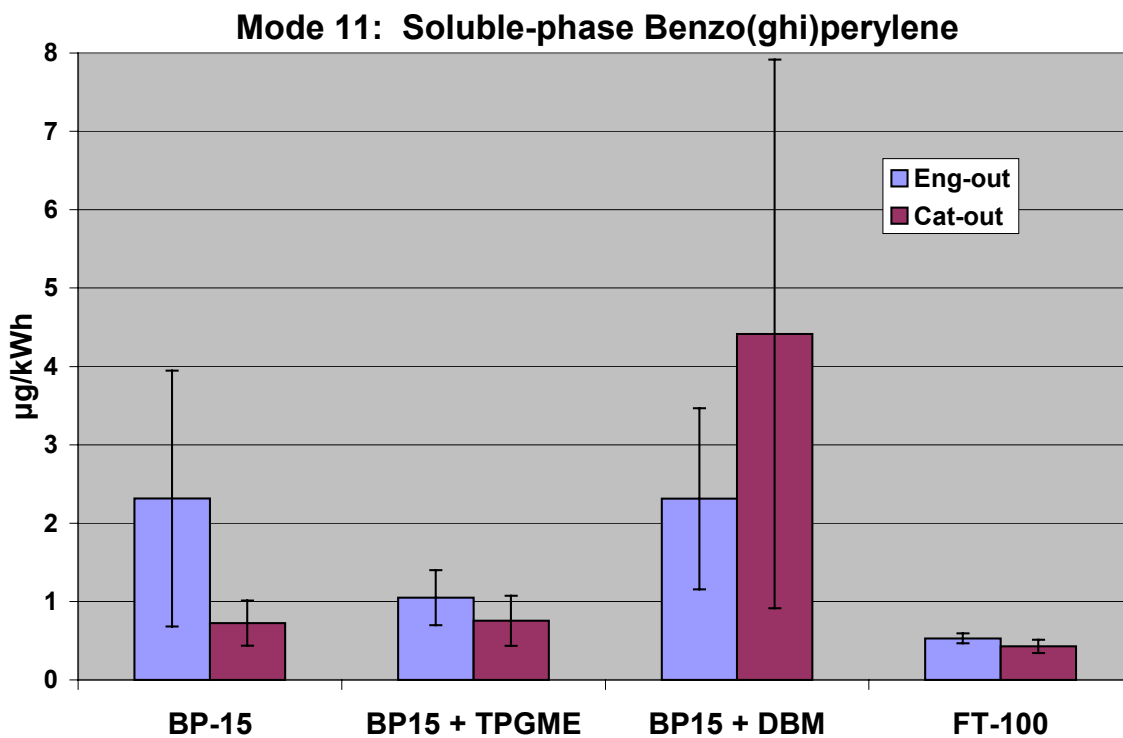


Figure C-29. Soluble-Phase Benzo(ghi)perylene Emissions by Fuel Type, Mode 11

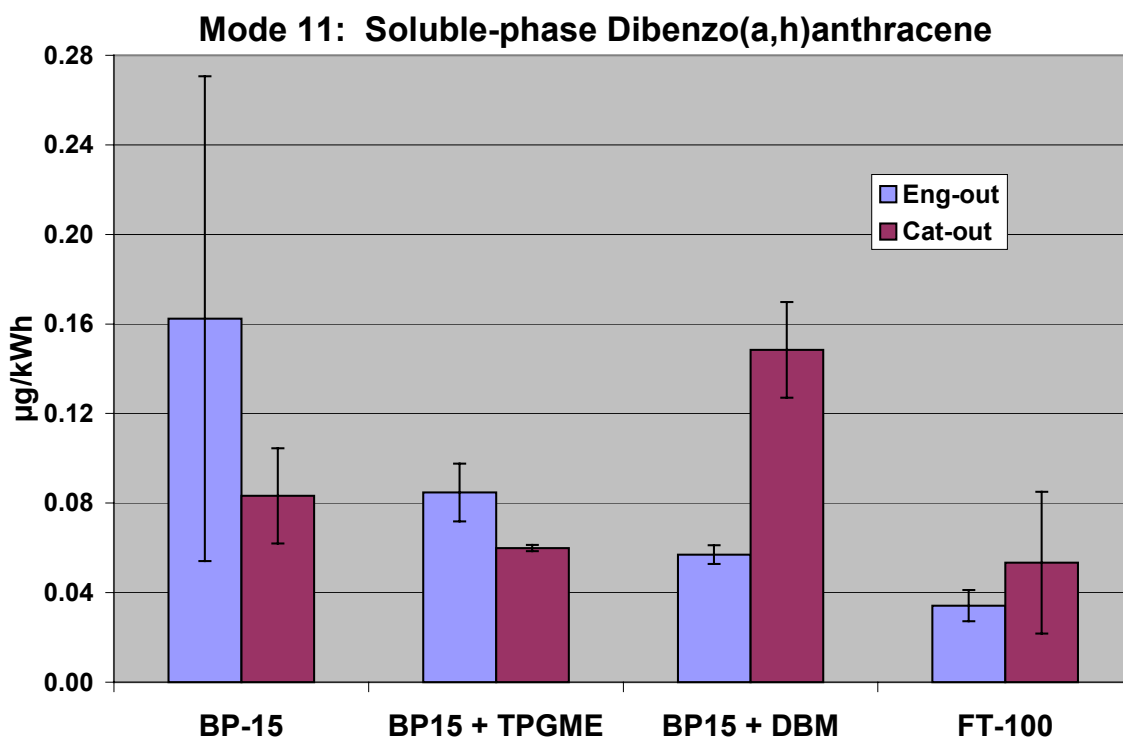


Figure C-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions by Fuel Type, Mode 11

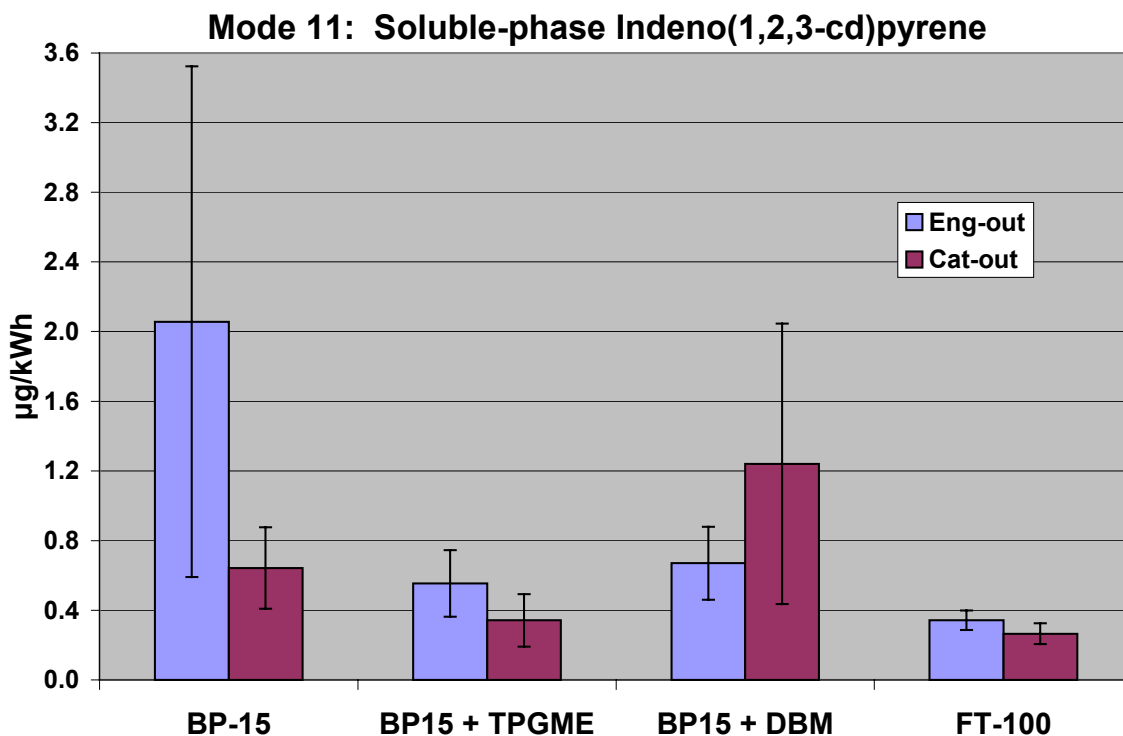


Figure C-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions by Fuel Type, Mode 11

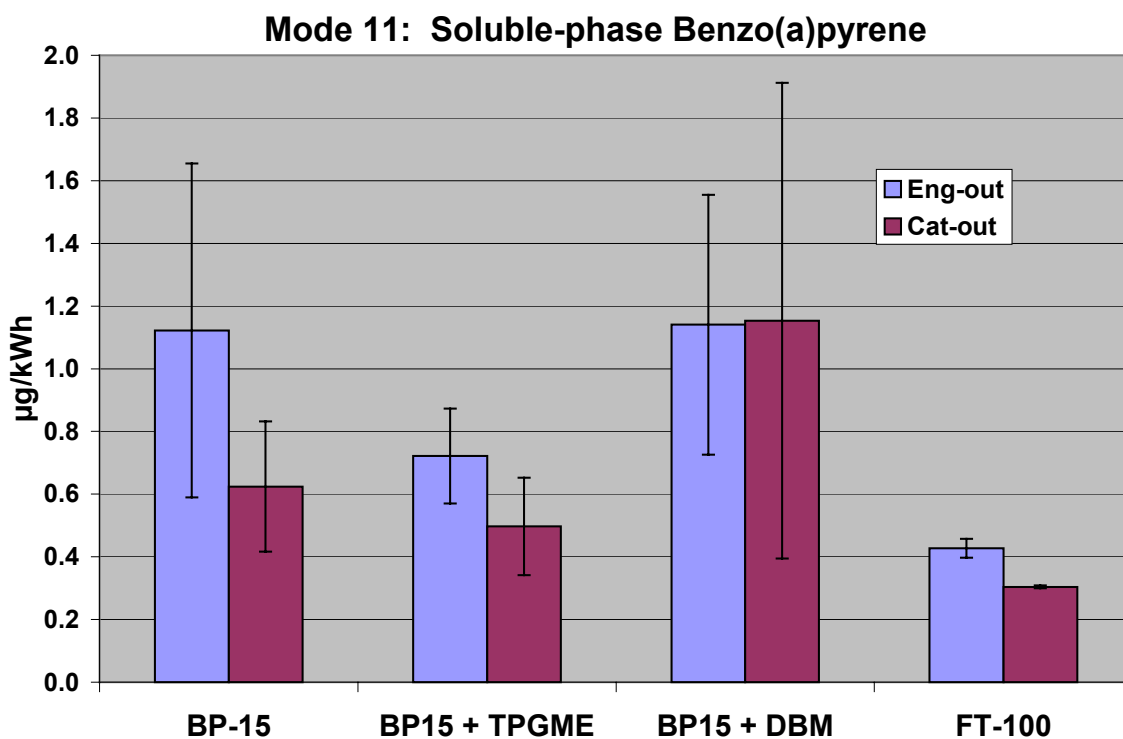


Figure C-32. Soluble-Phase Benzo(a)pyrene Emissions by Fuel Type, Mode 11



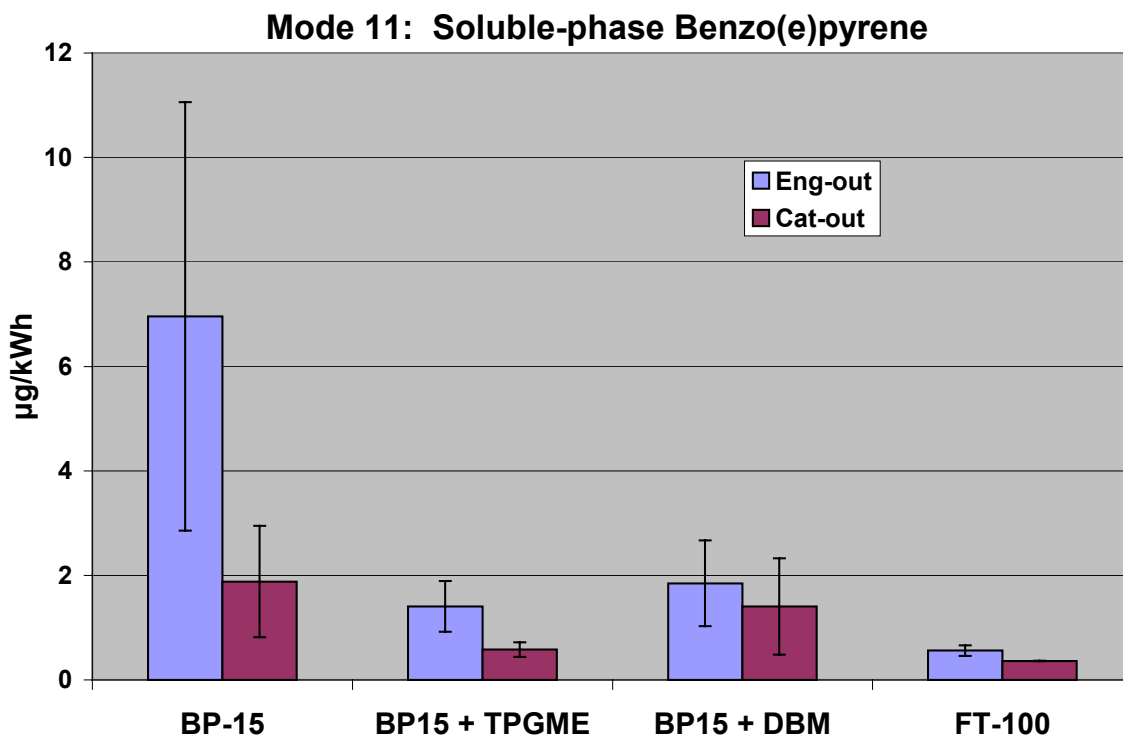


Figure C-33. Soluble-Phase Benzo(e)pyrene Emissions by Fuel Type, Mode 11

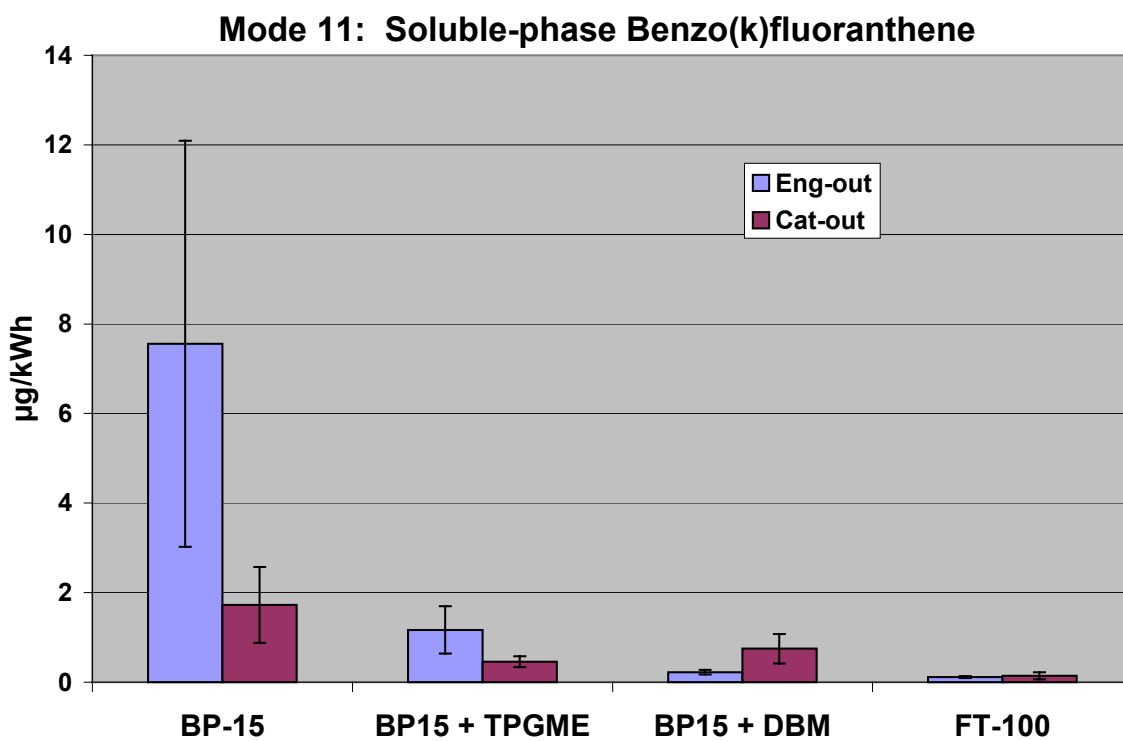


Figure C-34. Soluble-Phase Benzo(k)fluoranthene Emissions by Fuel Type, Mode 11

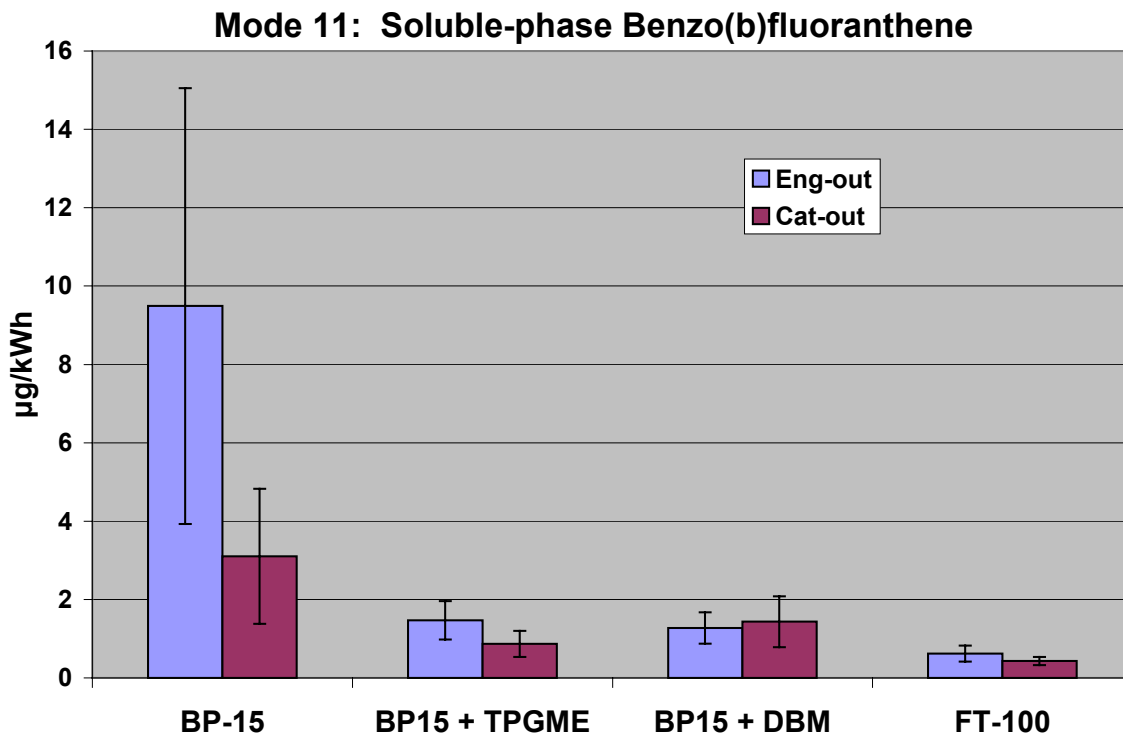


Figure C-35. Soluble-Phase Benzo(b)fluoranthene Emissions by Fuel Type, Mode 11

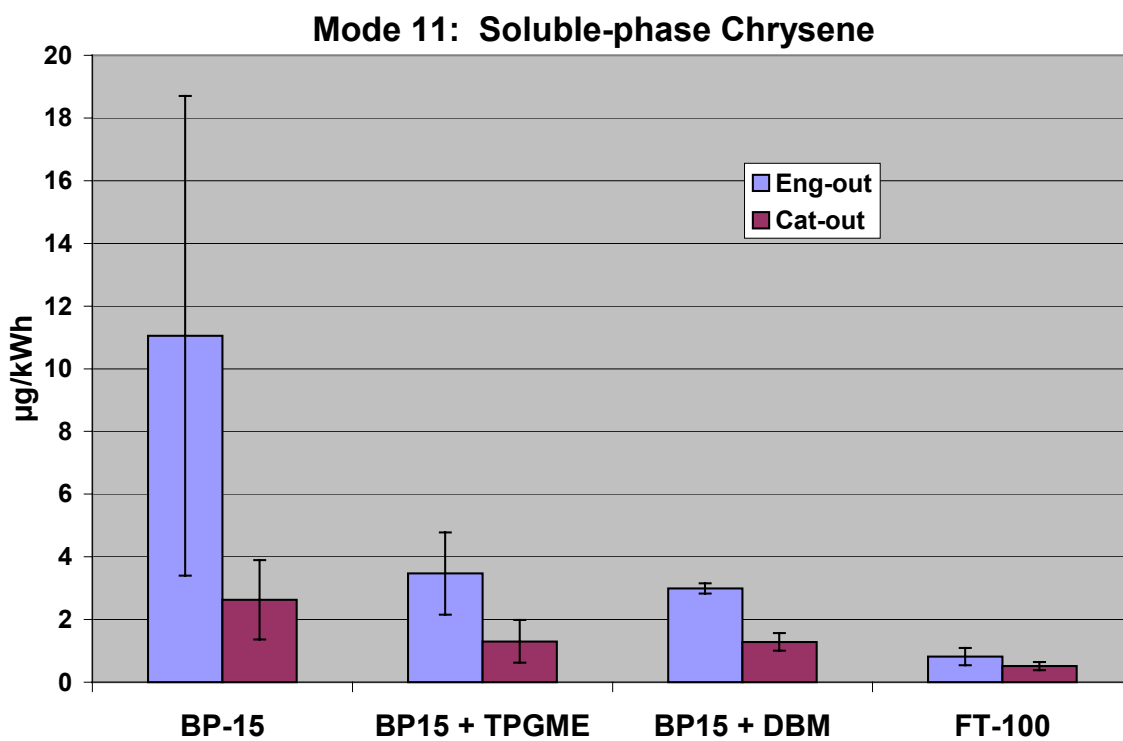


Figure C-36. Soluble-Phase Chrysene Emissions by Fuel Type, Mode 11

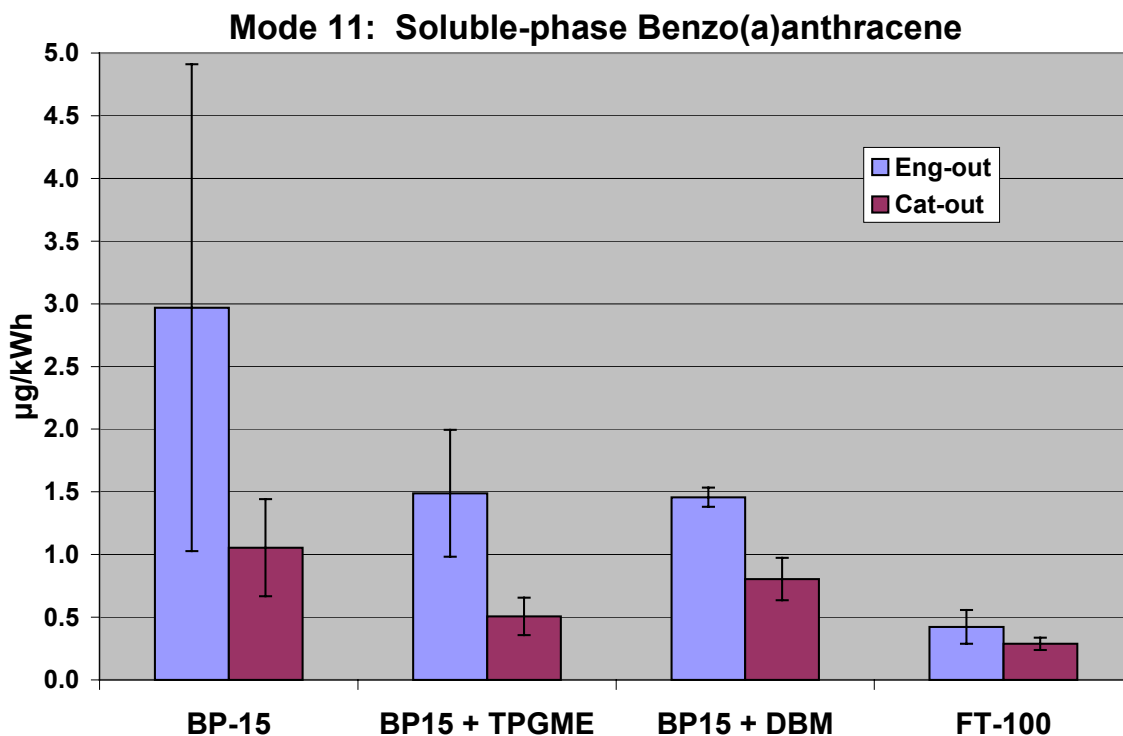


Figure C-37. Soluble-Phase Benzo(a)anthracene Emissions by Fuel Type, Mode 11

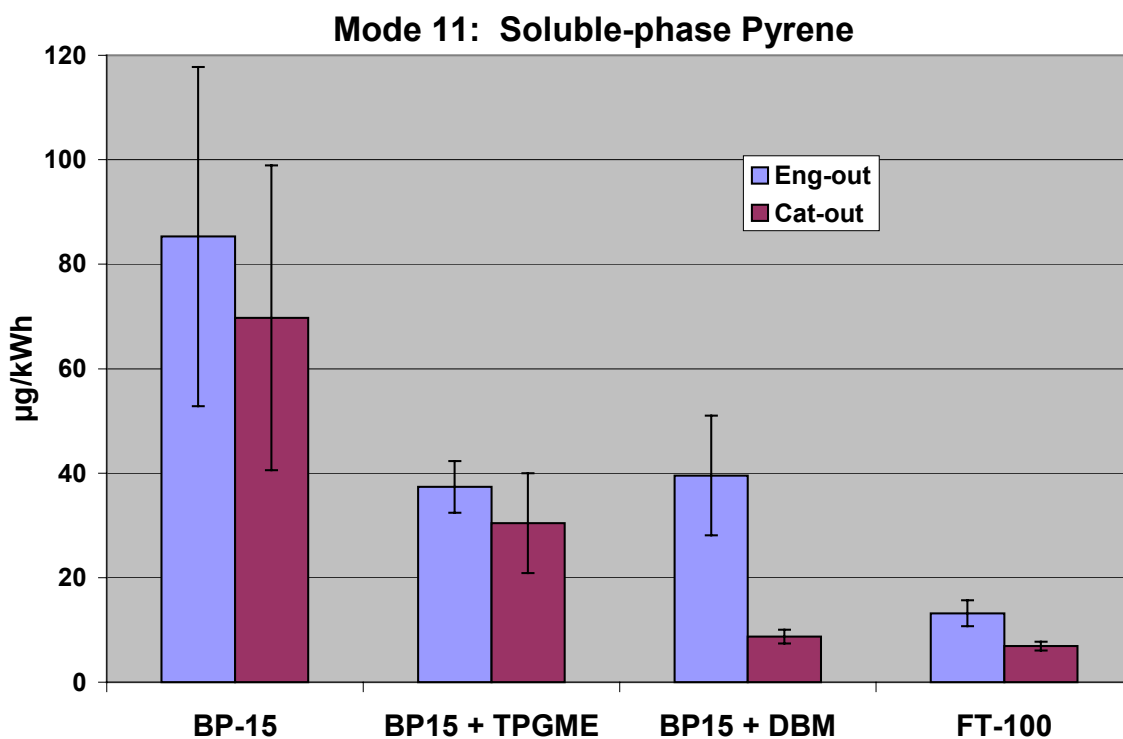


Figure C-38. Soluble-Phase Pyrene Emissions by Fuel Type, Mode 11

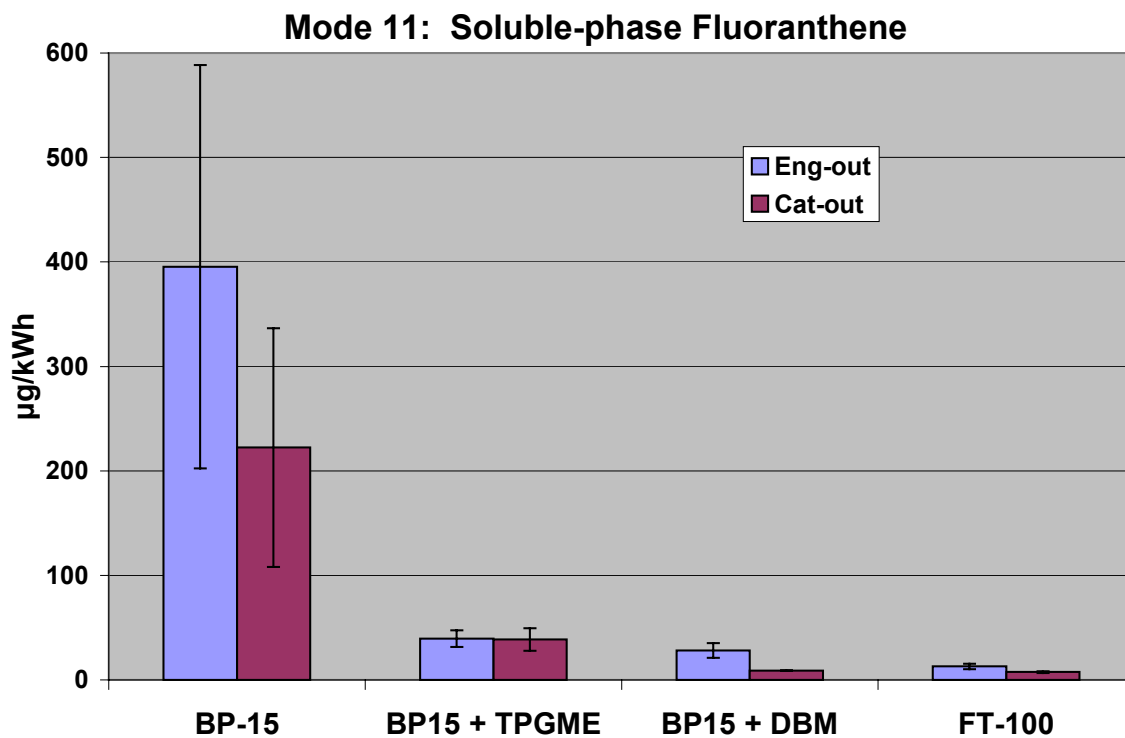


Figure C-39. Soluble-Phase Fluoranthene Emissions by Fuel Type, Mode 11

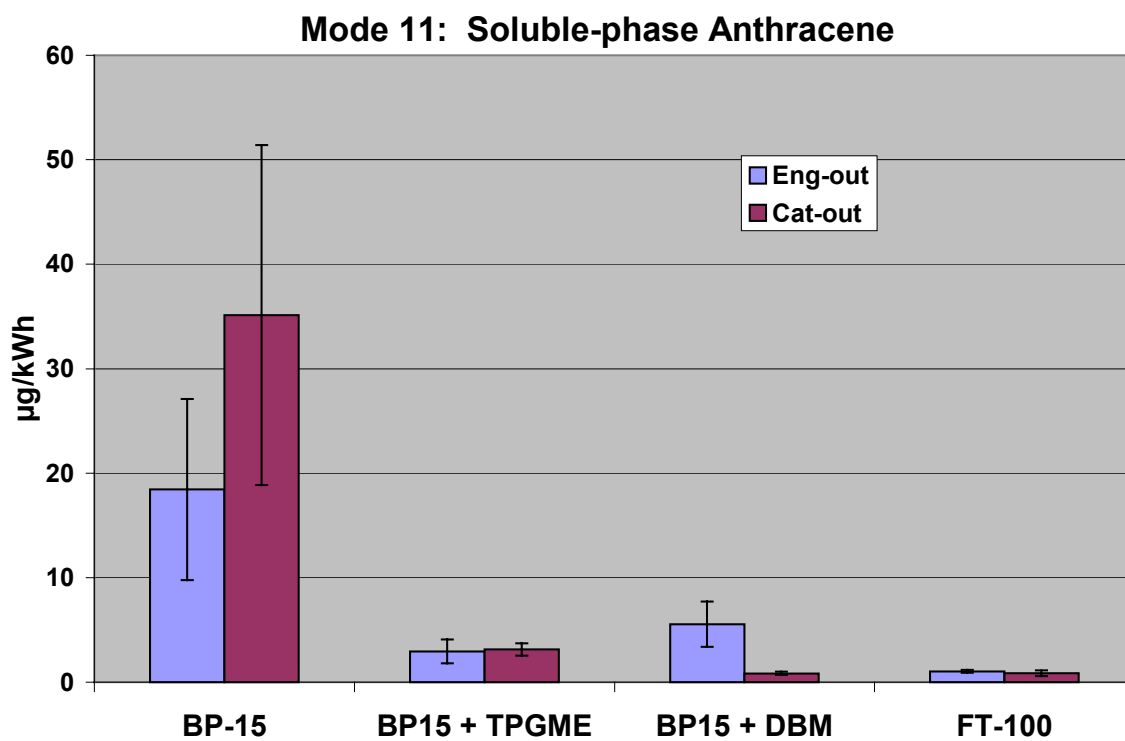


Figure C-40. Soluble-Phase Anthracene Emissions by Fuel Type, Mode 11

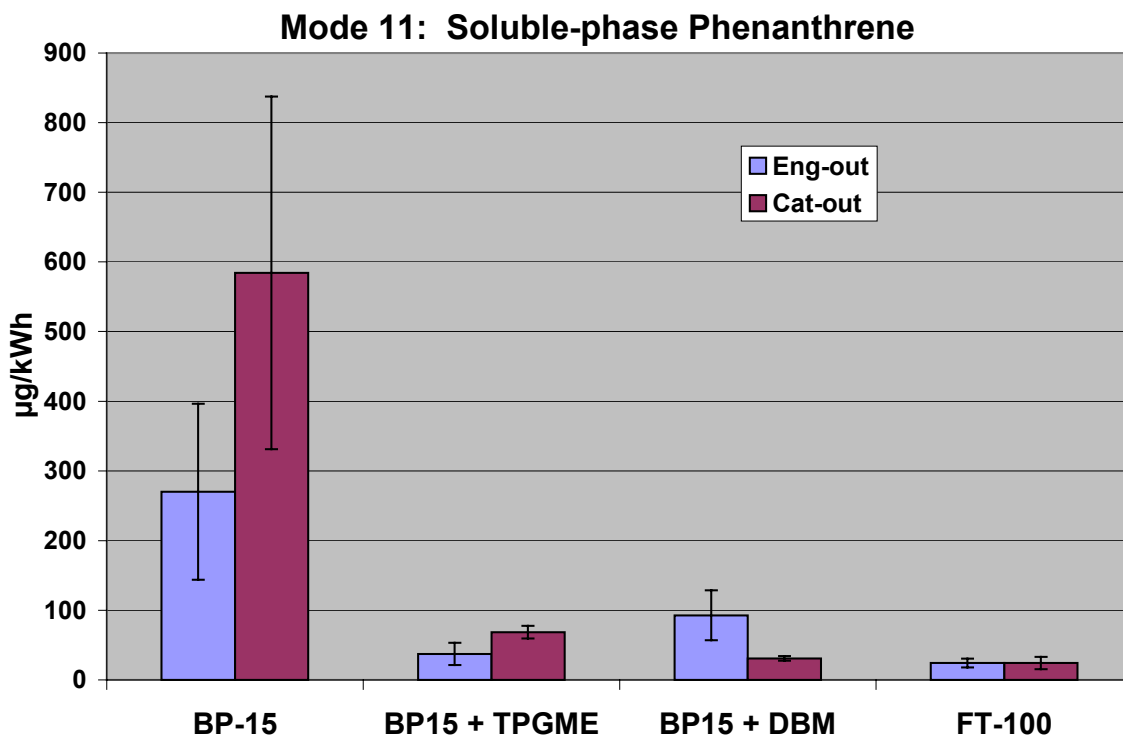


Figure C-41. Soluble-Phase Phenanthrene Emissions by Fuel Type, Mode 11

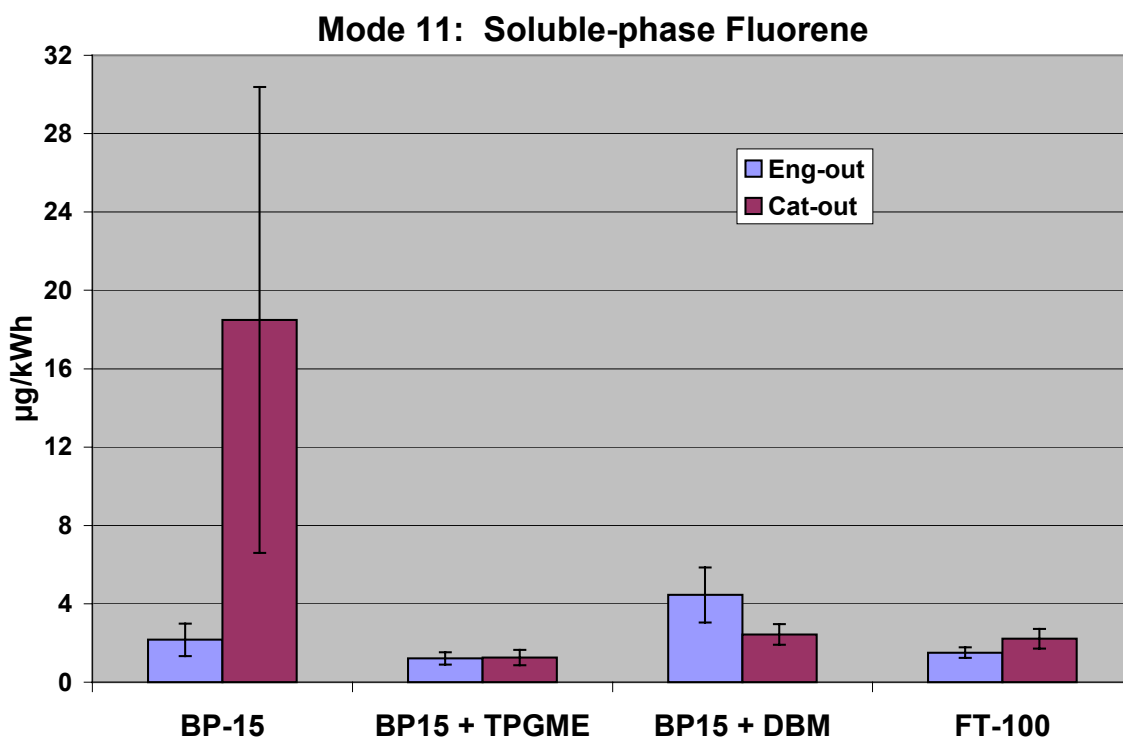


Figure C-42. Soluble-Phase Fluorene Emissions by Fuel Type, Mode 11

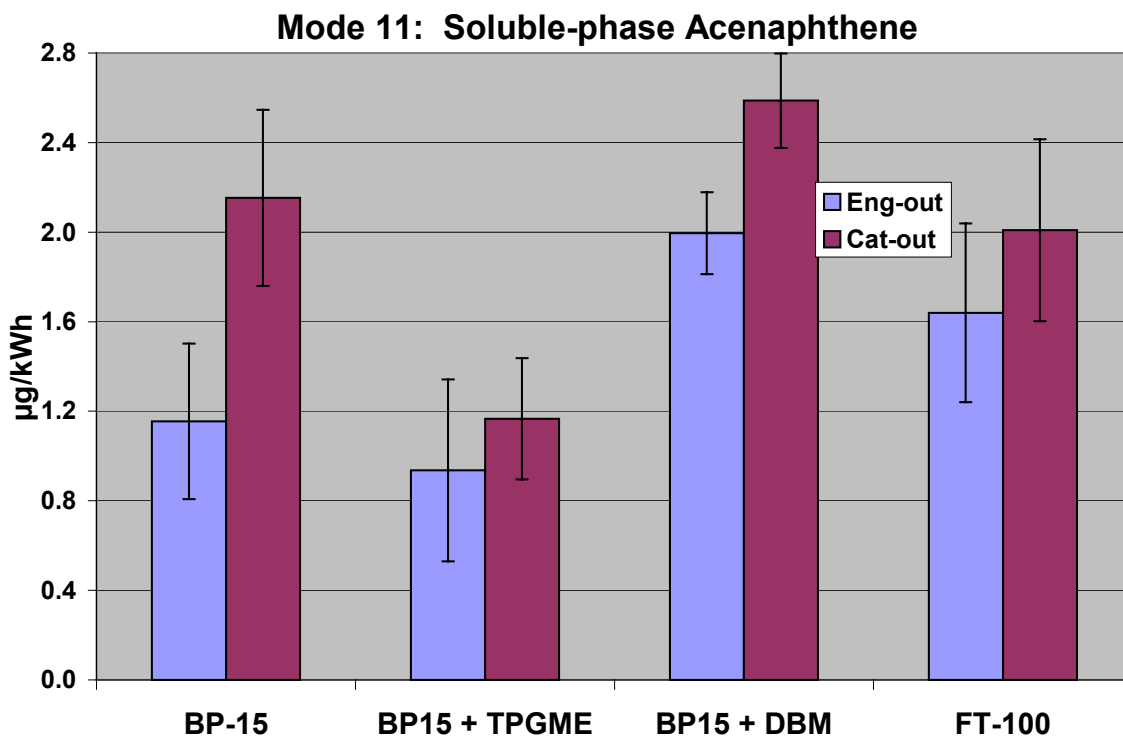


Figure C-43. Soluble-Phase Acenaphthene Emissions by Fuel Type, Mode 11

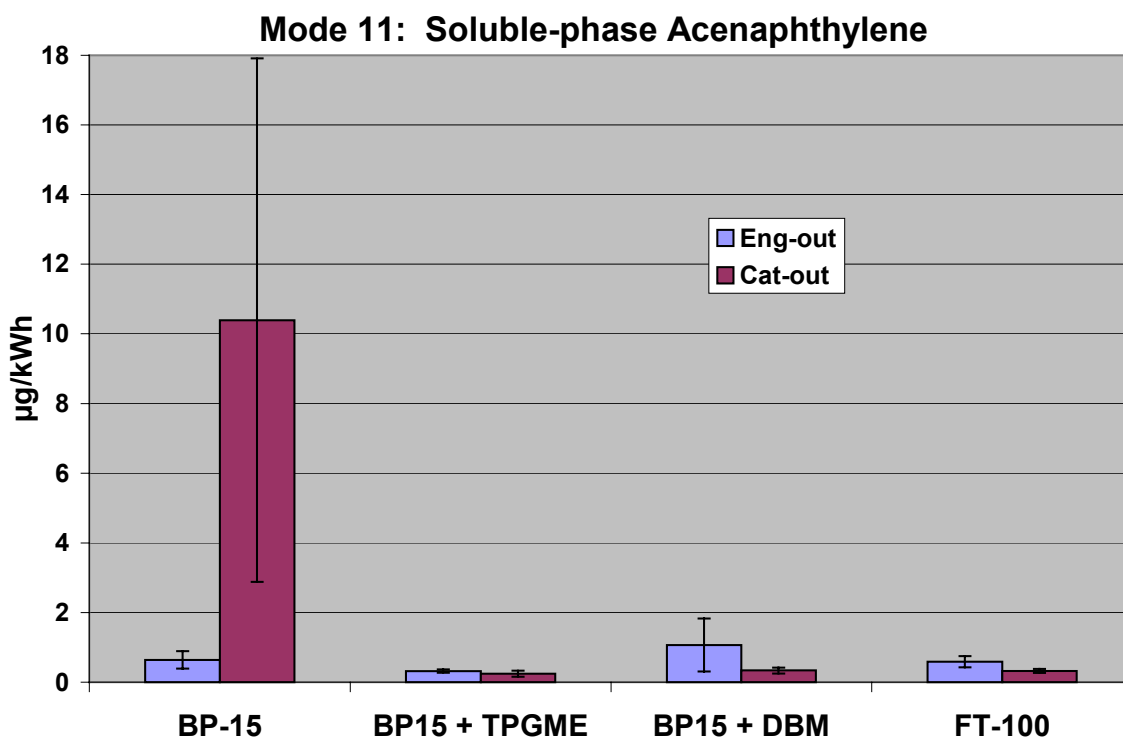


Figure C-44. Soluble-Phase Acenaphthylene Emissions by Fuel Type, Mode 11

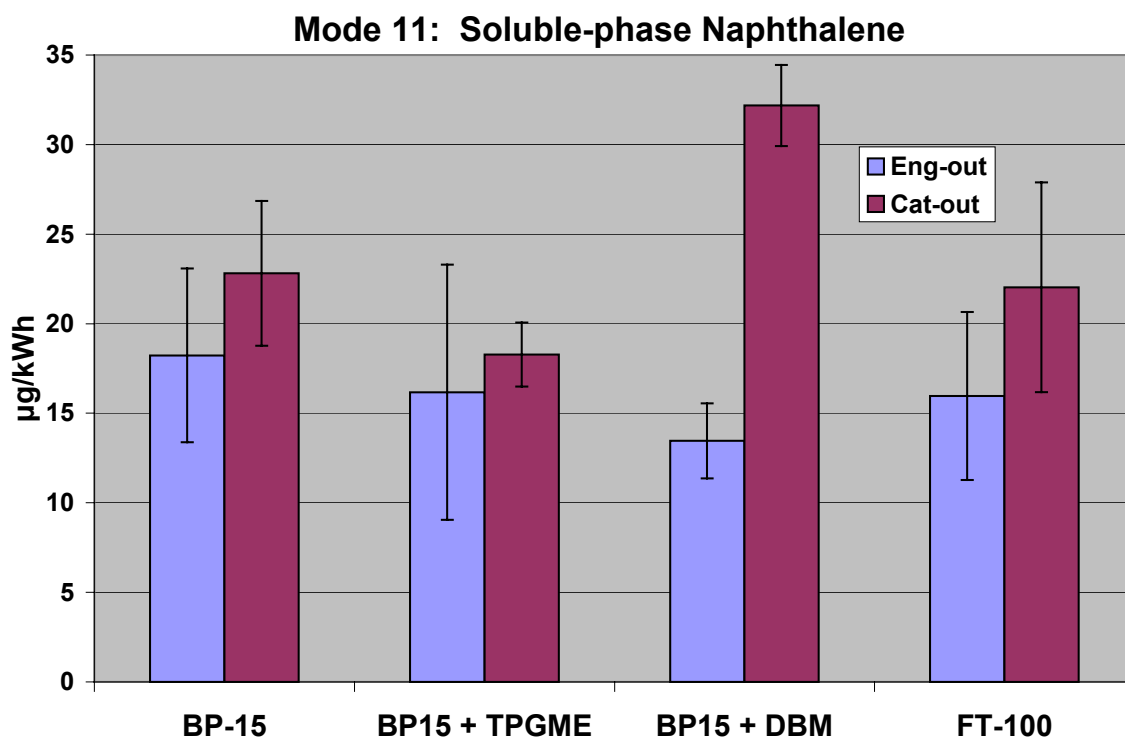


Figure C-45. Soluble-Phase Naphthalene Emissions by Fuel Type, Mode 11

## **APPENDIX D**

### **Mode 22 Operation Test Results**



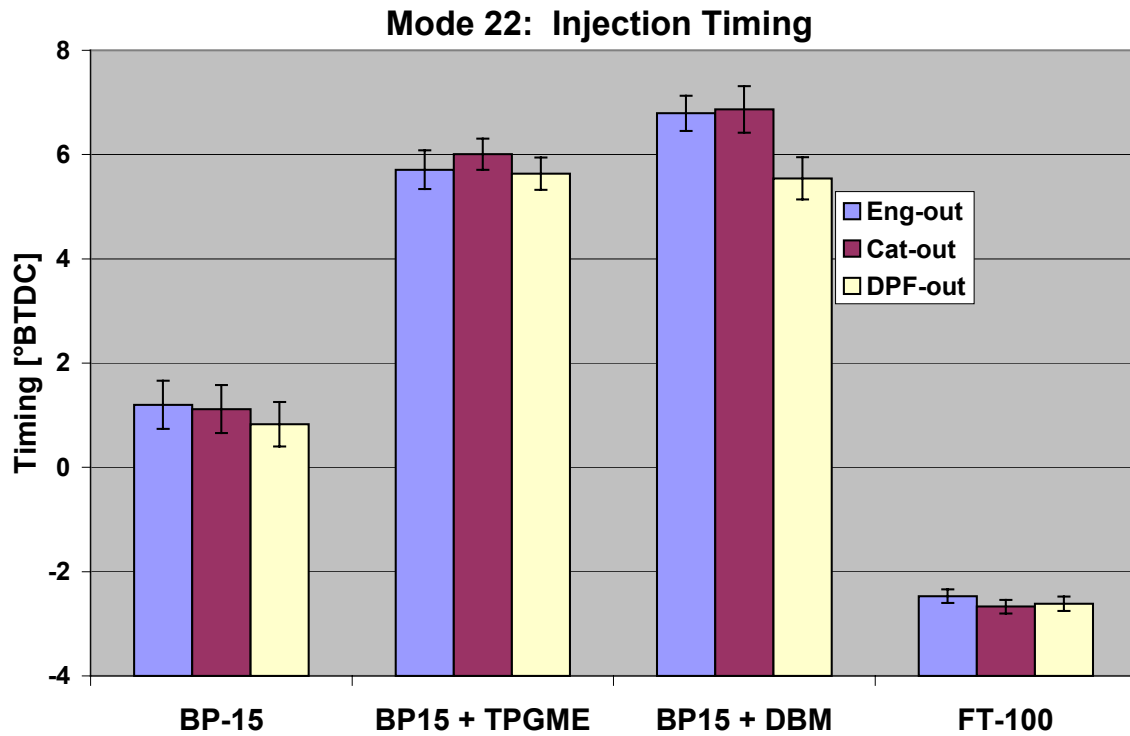


Figure D-1. Injection Timing by Fuel Type, Mode 22

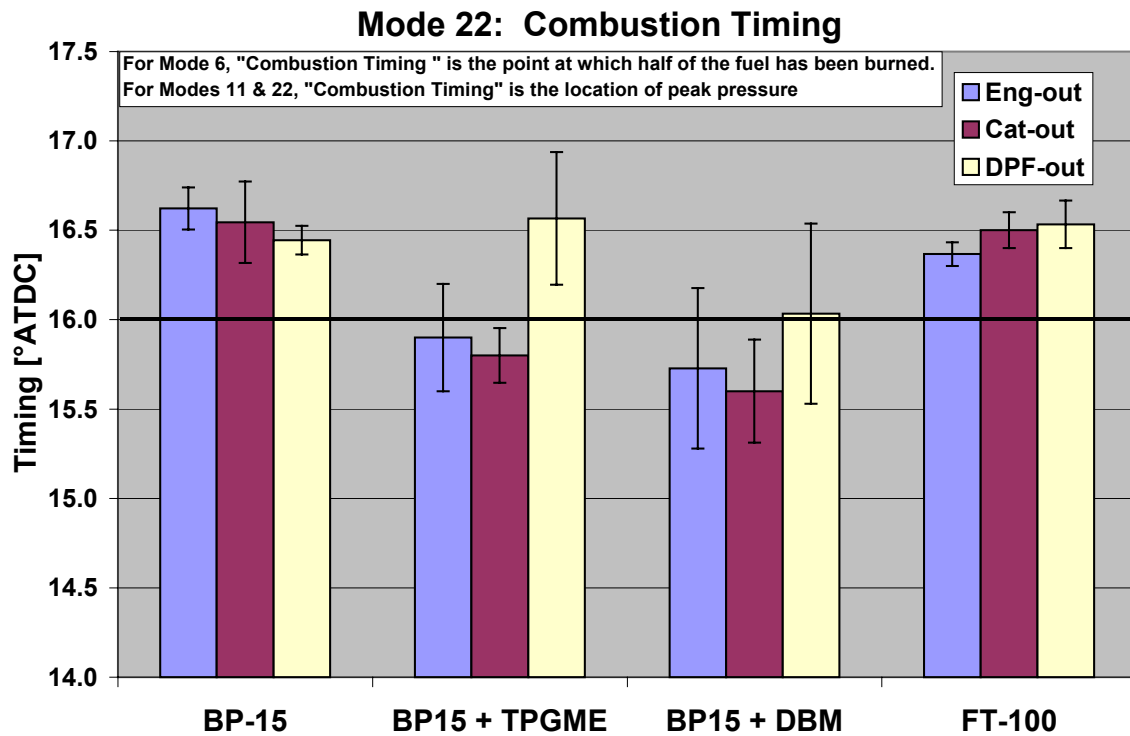


Figure D-2. Combustion Timing by Fuel Type, Mode 22

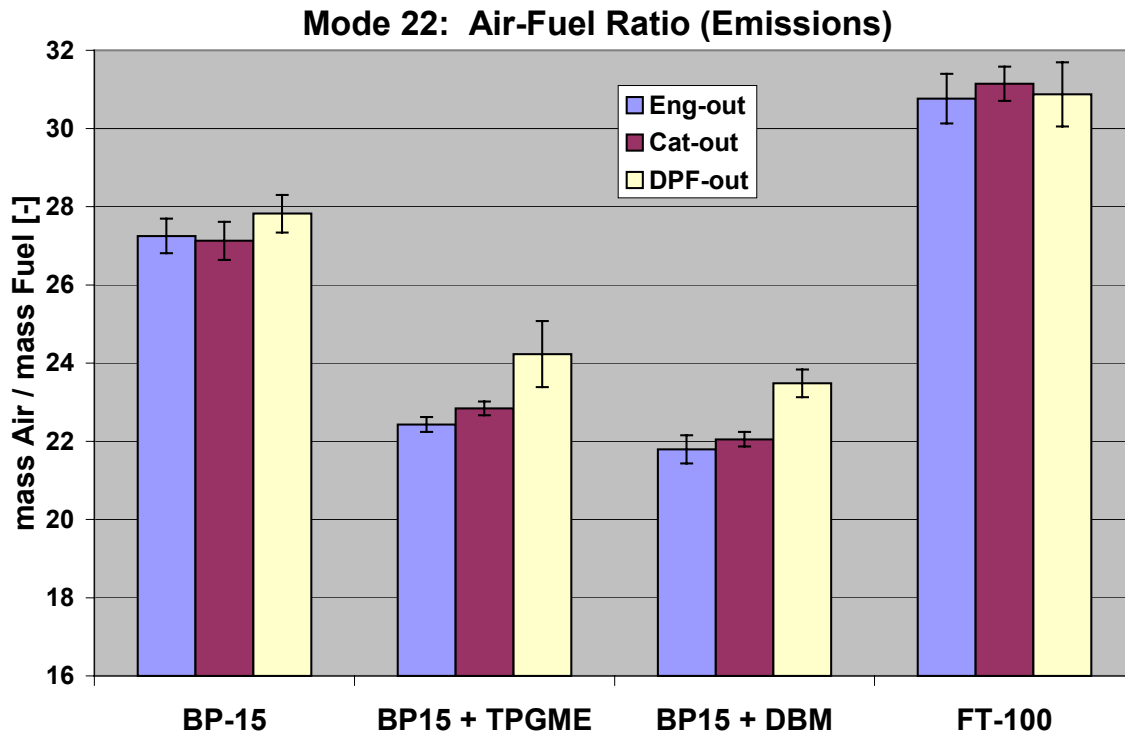


Figure D-3. Emissions Air-Fuel Ratio by Fuel Type, Mode 22

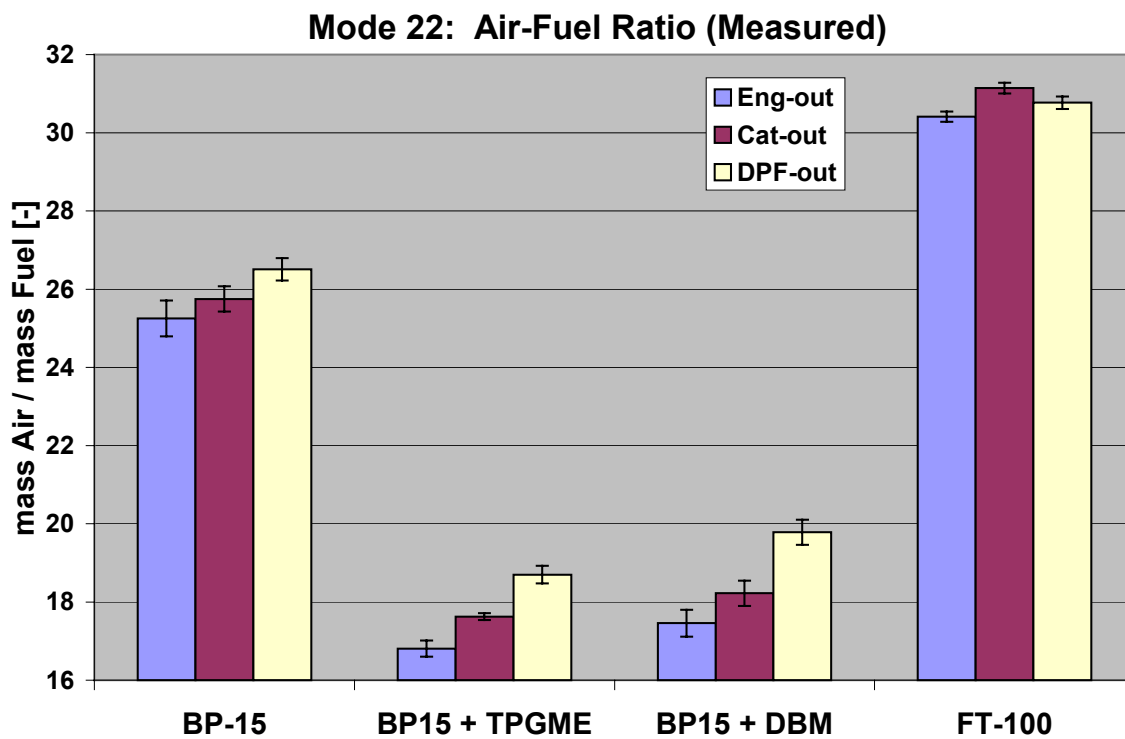


Figure D-4. Measured Air-Fuel Ratio by Fuel Type, Mode 22

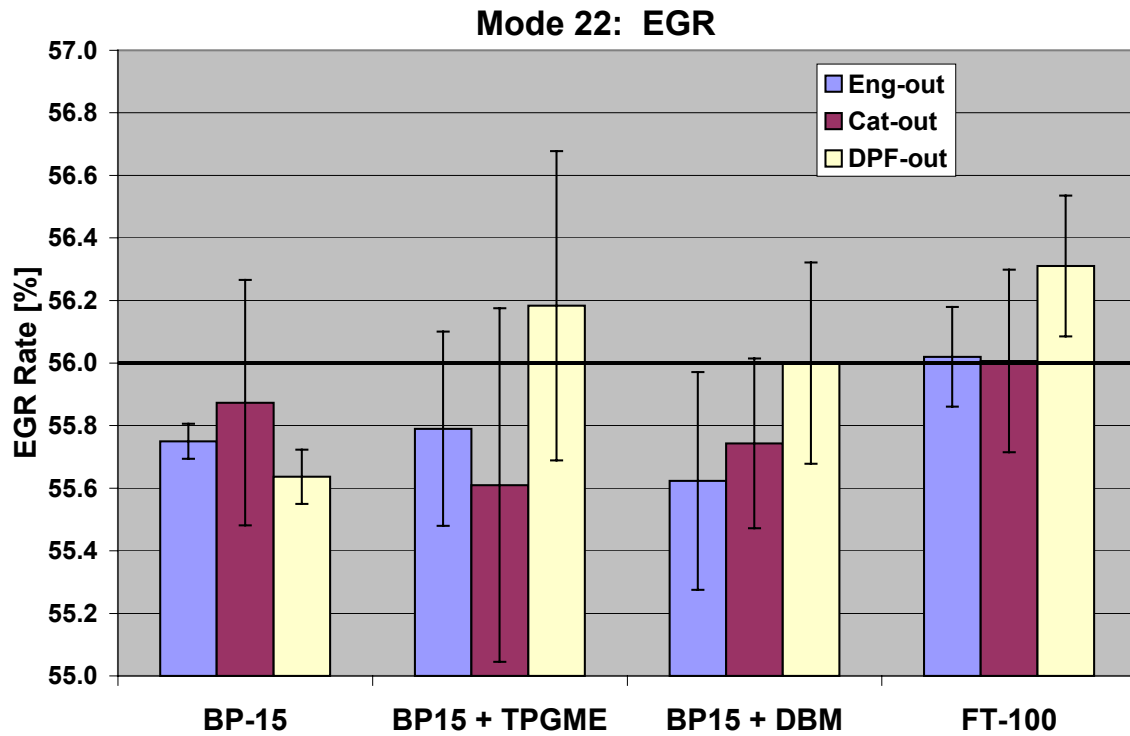


Figure D-5. EGR Rate by Fuel Type, Mode 22

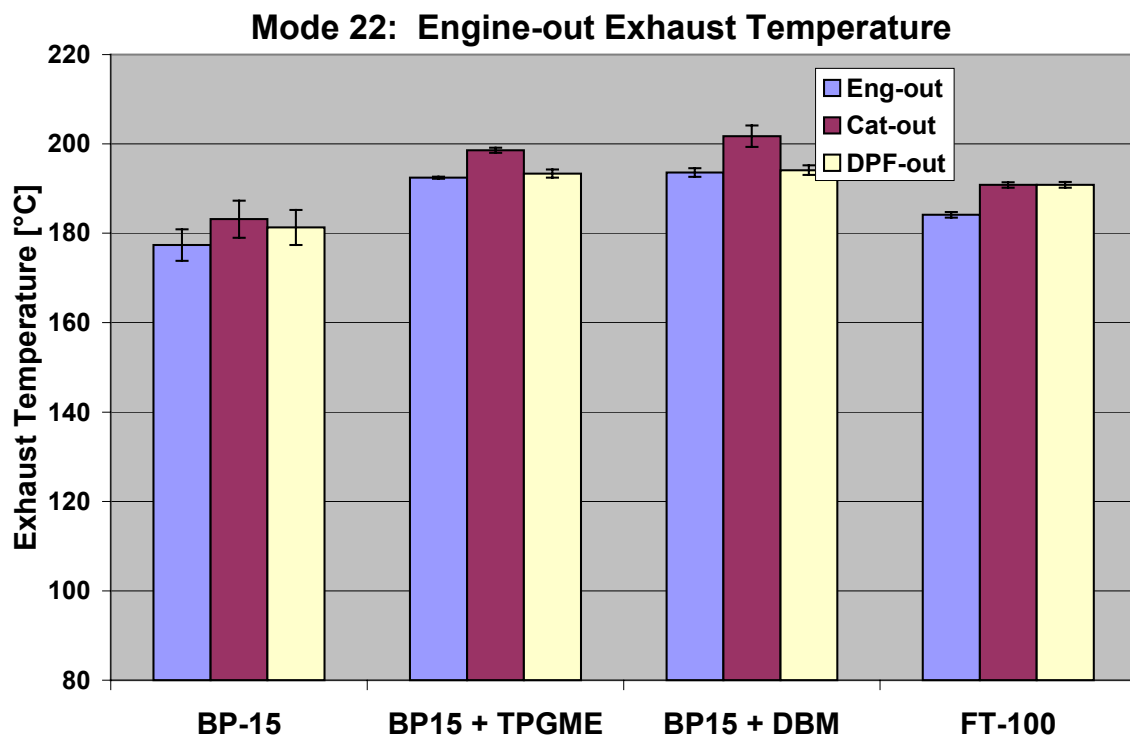


Figure D-6. Engine-Out Exhaust Temperature by Fuel Type, Mode 22

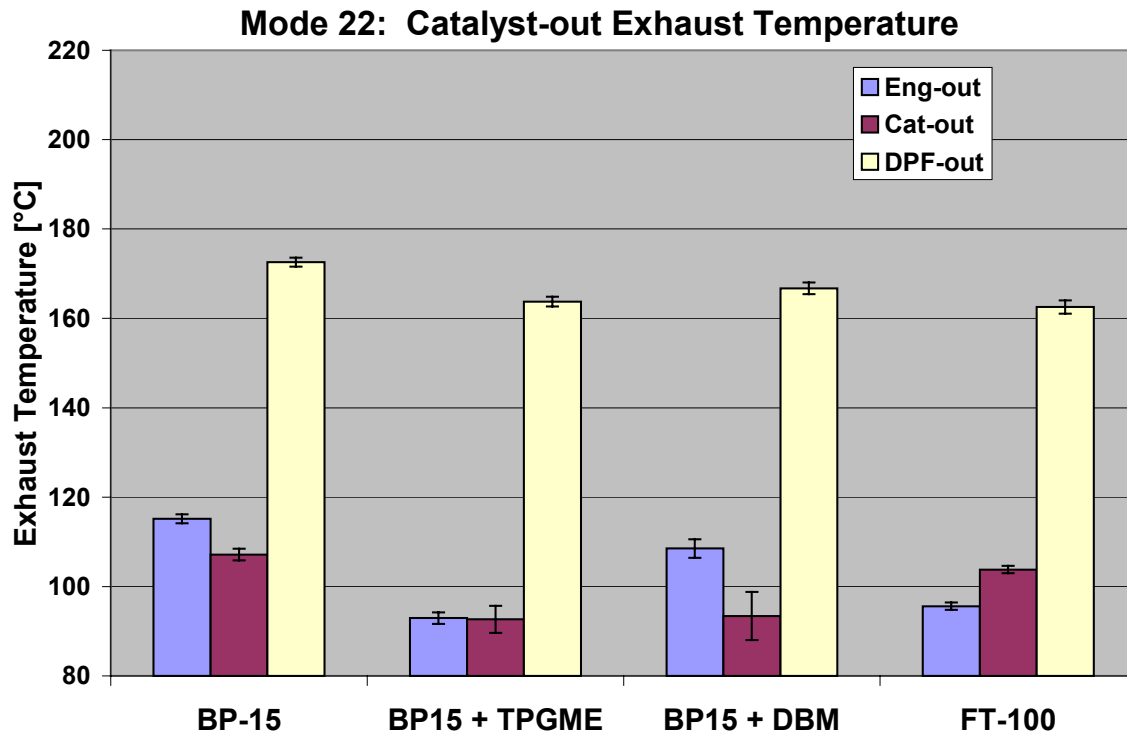


Figure D-7. Catalyst-Out Exhaust Temperature by Fuel Type, Mode 22

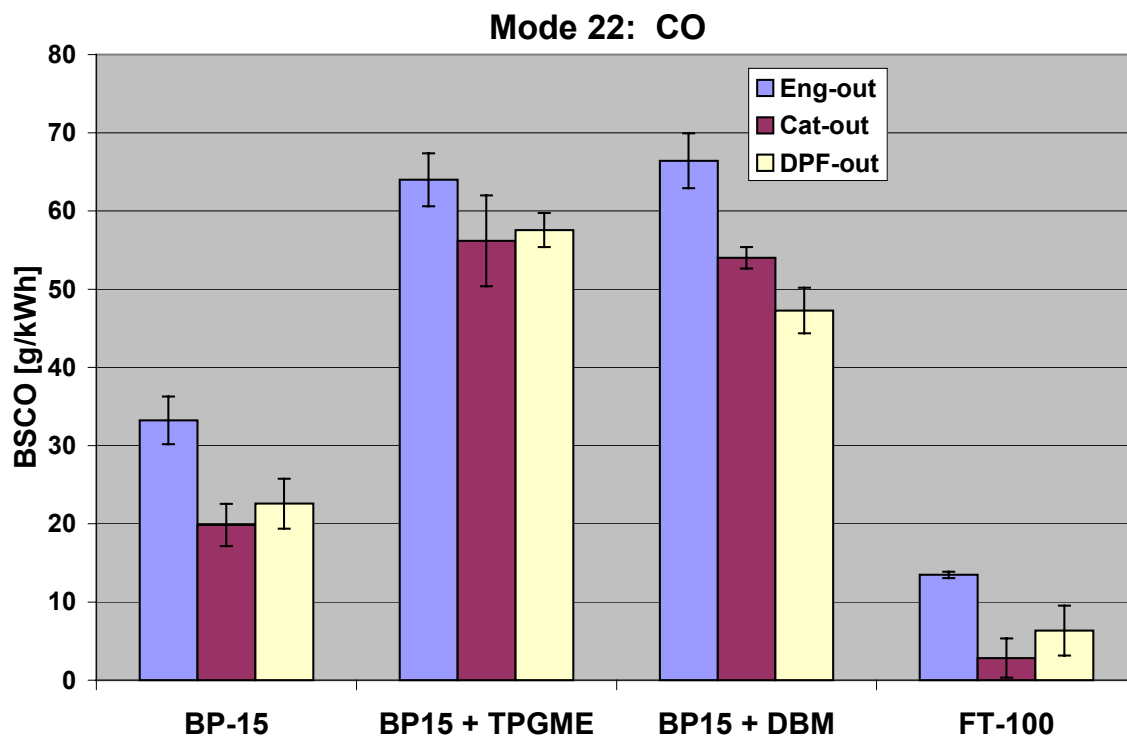


Figure D-8. Carbon Monoxide Emissions by Fuel Type, Mode 22

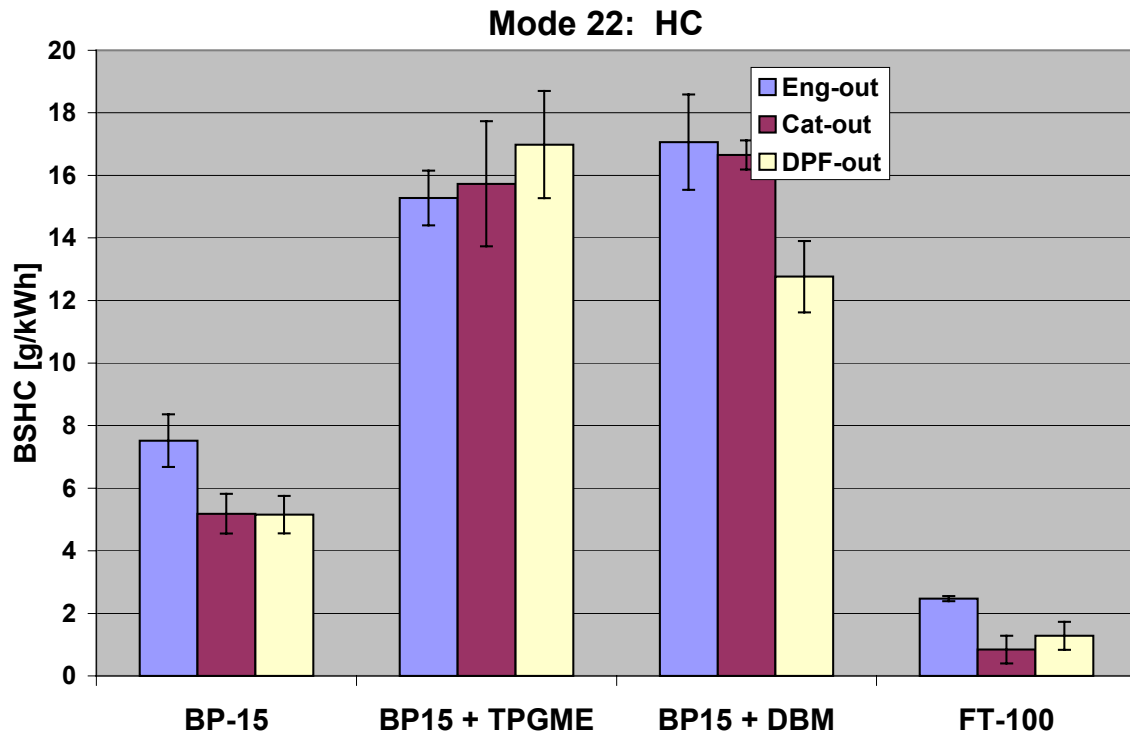


Figure D-9. Hydrocarbon Emissions by Fuel Type, Mode 22

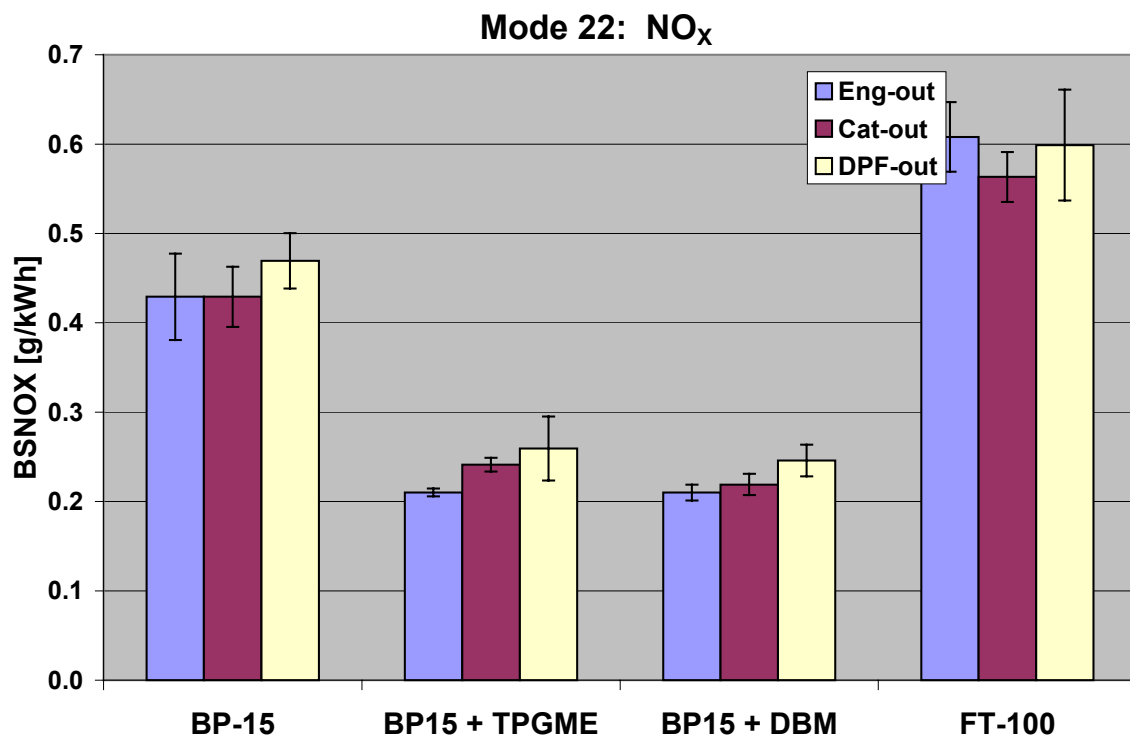


Figure D-10. Nitrogen Oxides Emissions by Fuel Type, Mode 22

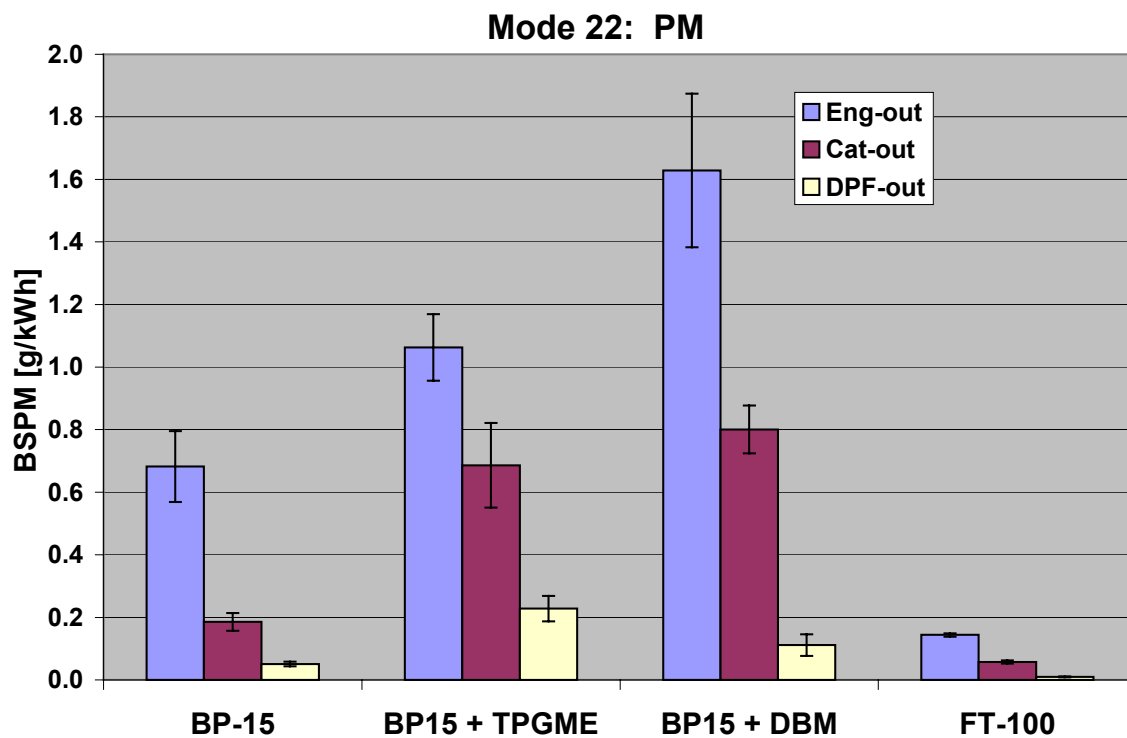


Figure D-11. Particulate Matter Emissions by Fuel Type, Mode 22

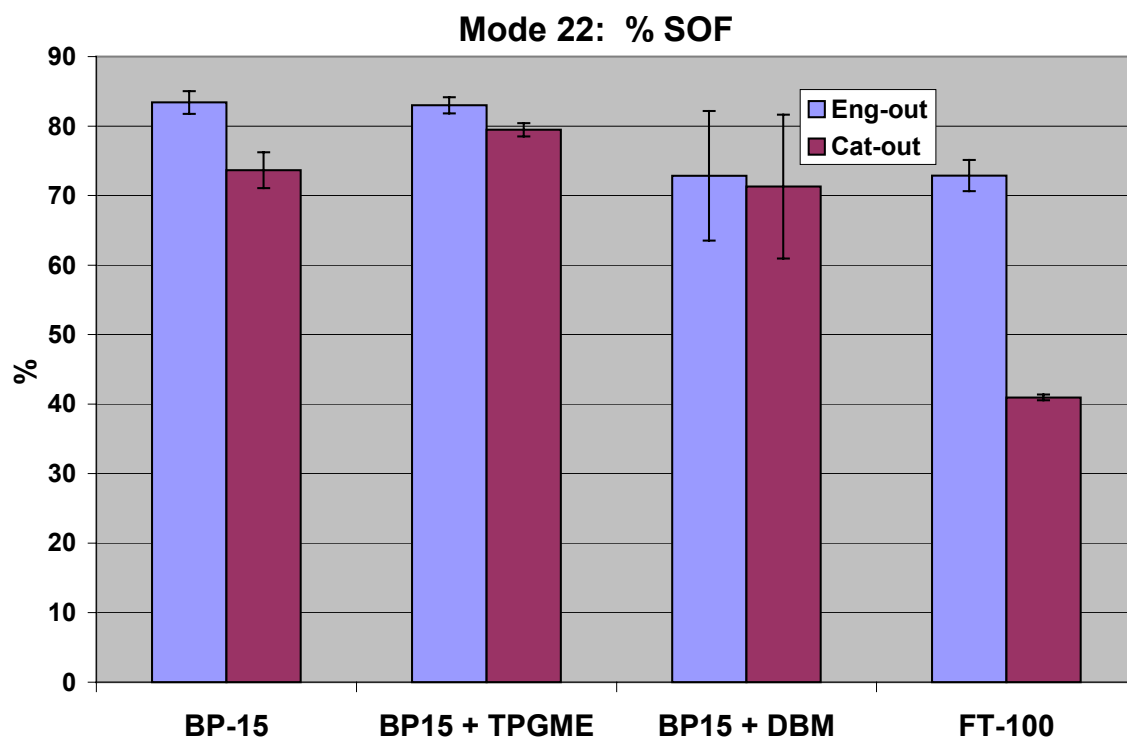


Figure D-12. Percent Soluble Organic Fraction by Fuel Type, Mode 22

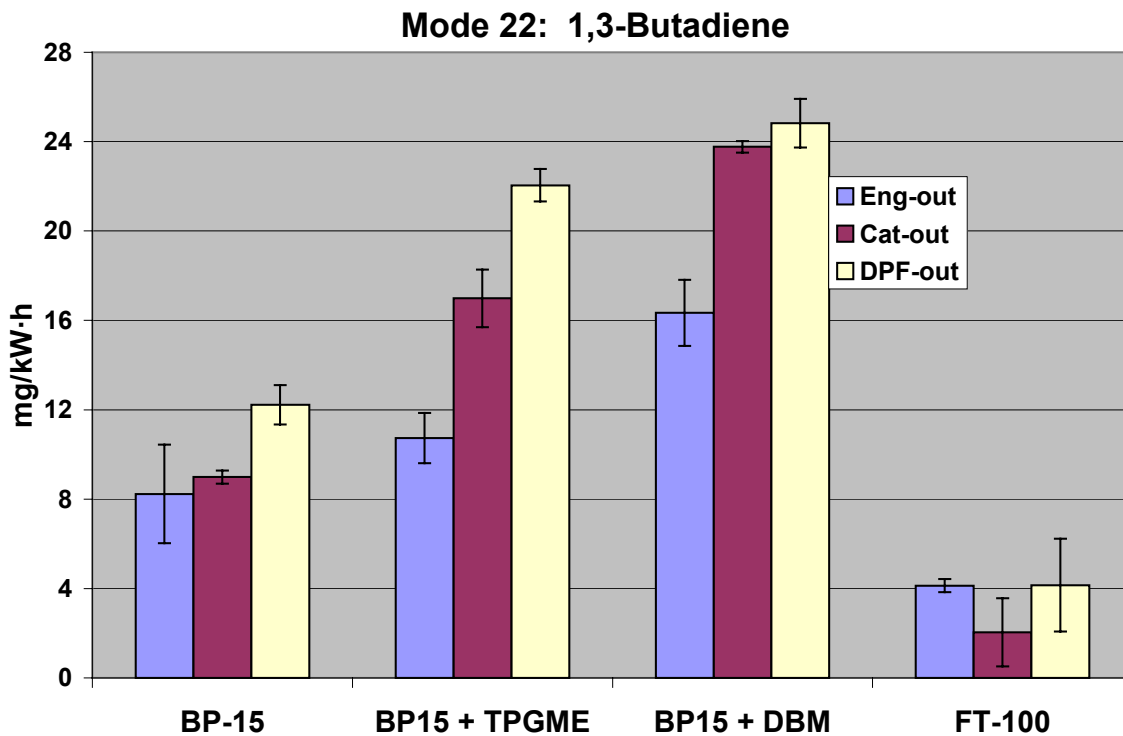


Figure D-13. 1,3-Butadiene Emissions by Fuel Type, Mode 22

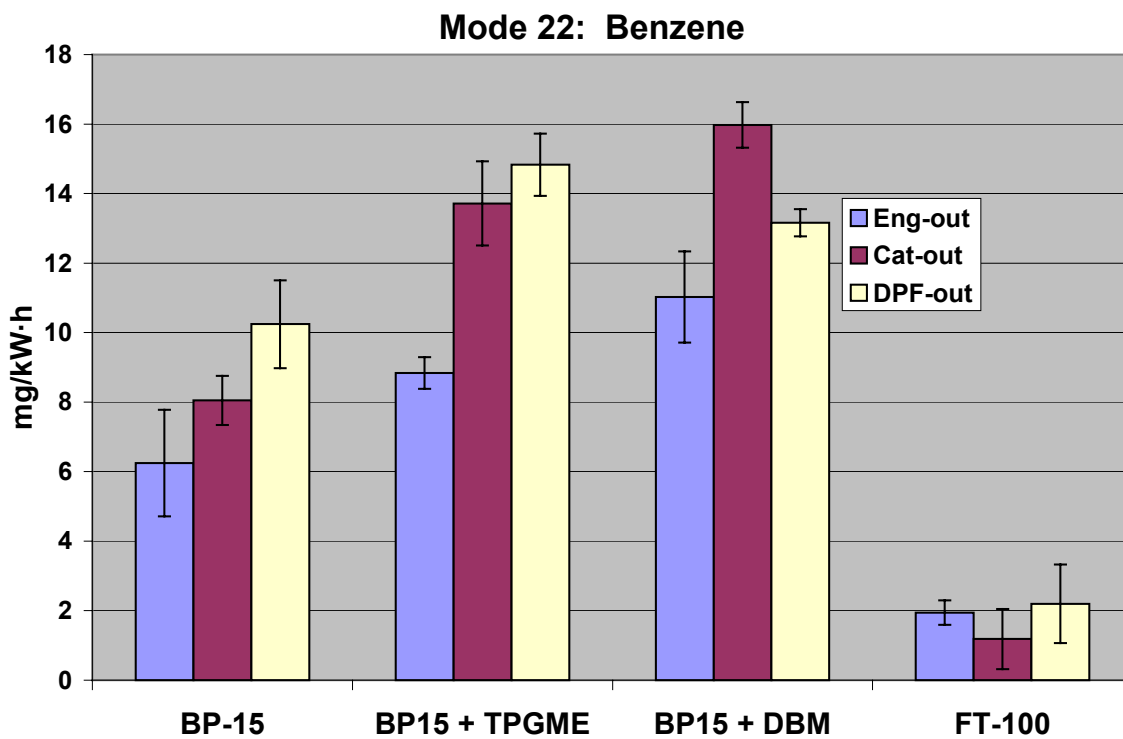


Figure D-14. Benzene Emissions by Fuel Type, Mode 22

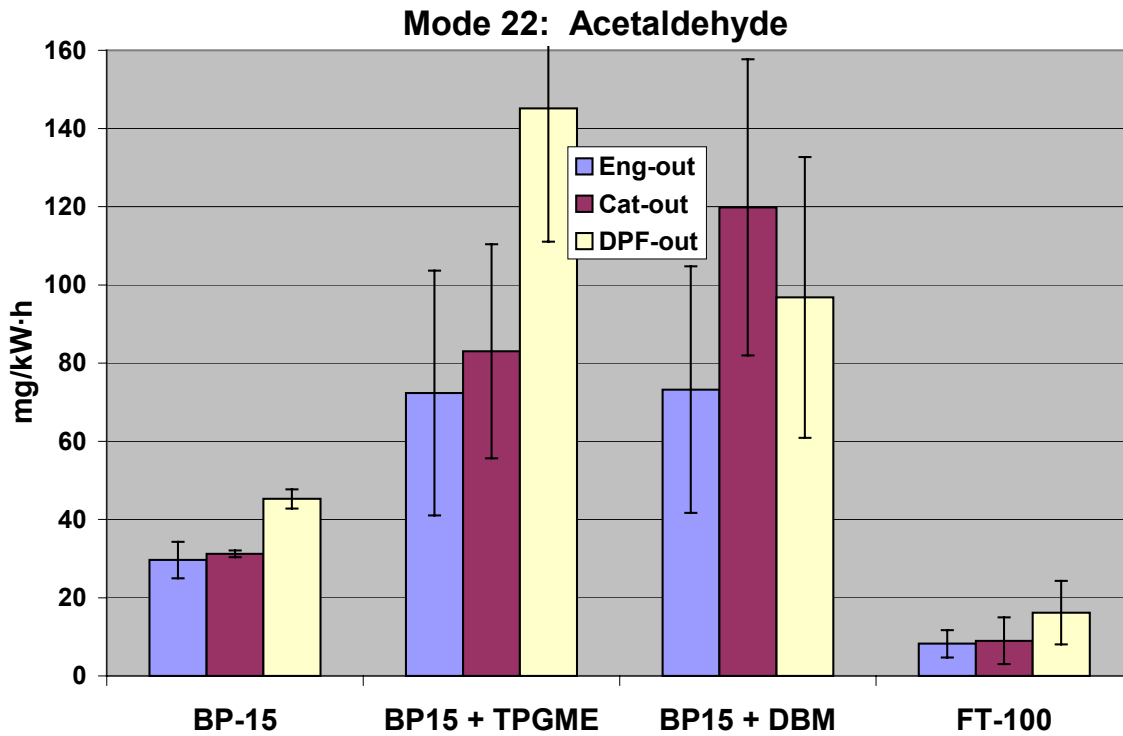


Figure D-15. Acetaldehyde Emissions by Fuel Type, Mode 22

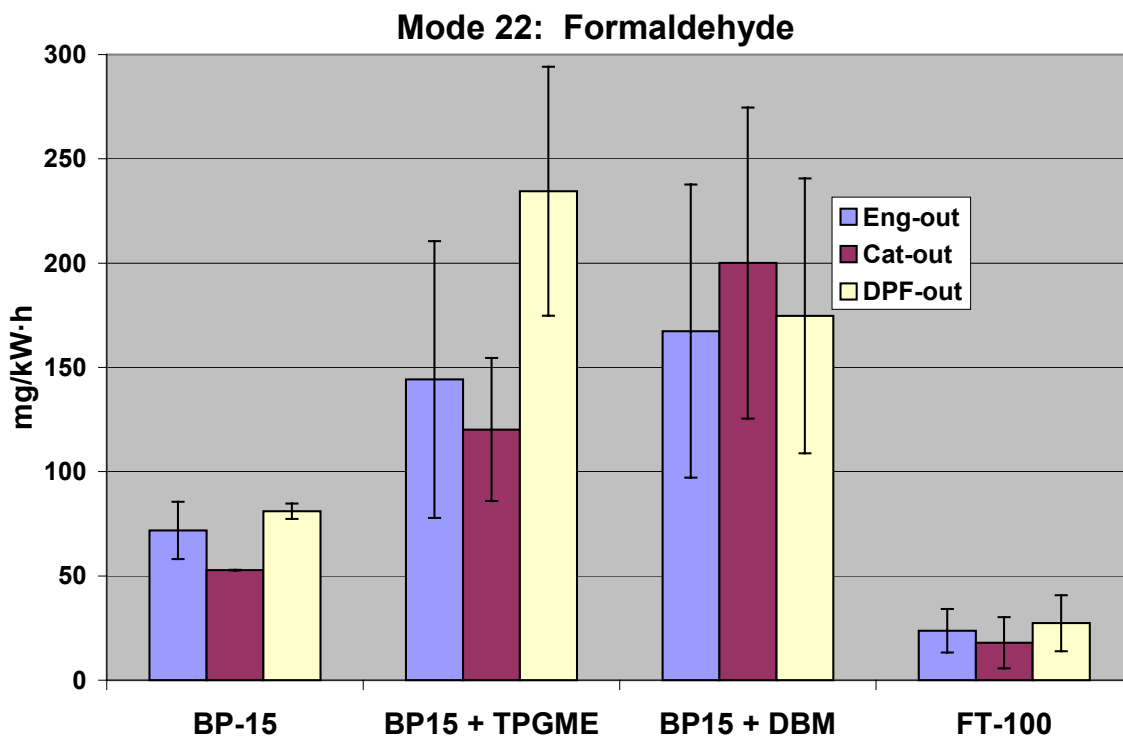


Figure D-16. Formaldehyde Emissions by Fuel Type, Mode 22



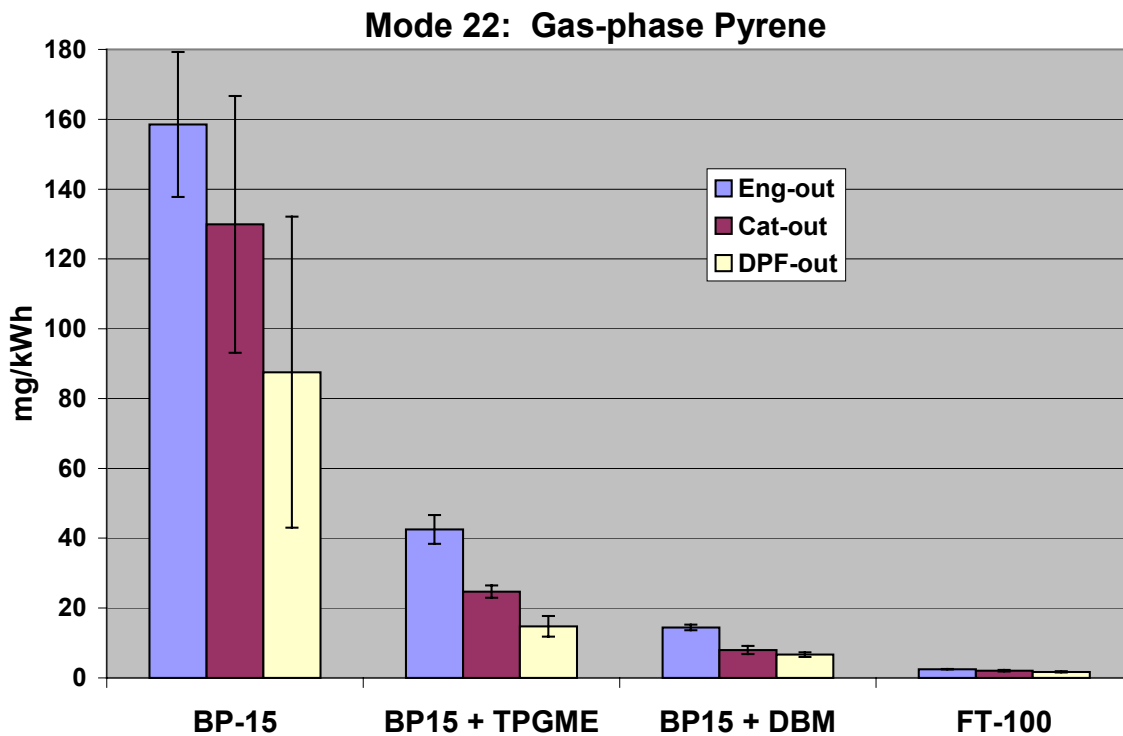


Figure D-17. Gas-Phase Pyrene Emissions by Fuel Type, Mode 22

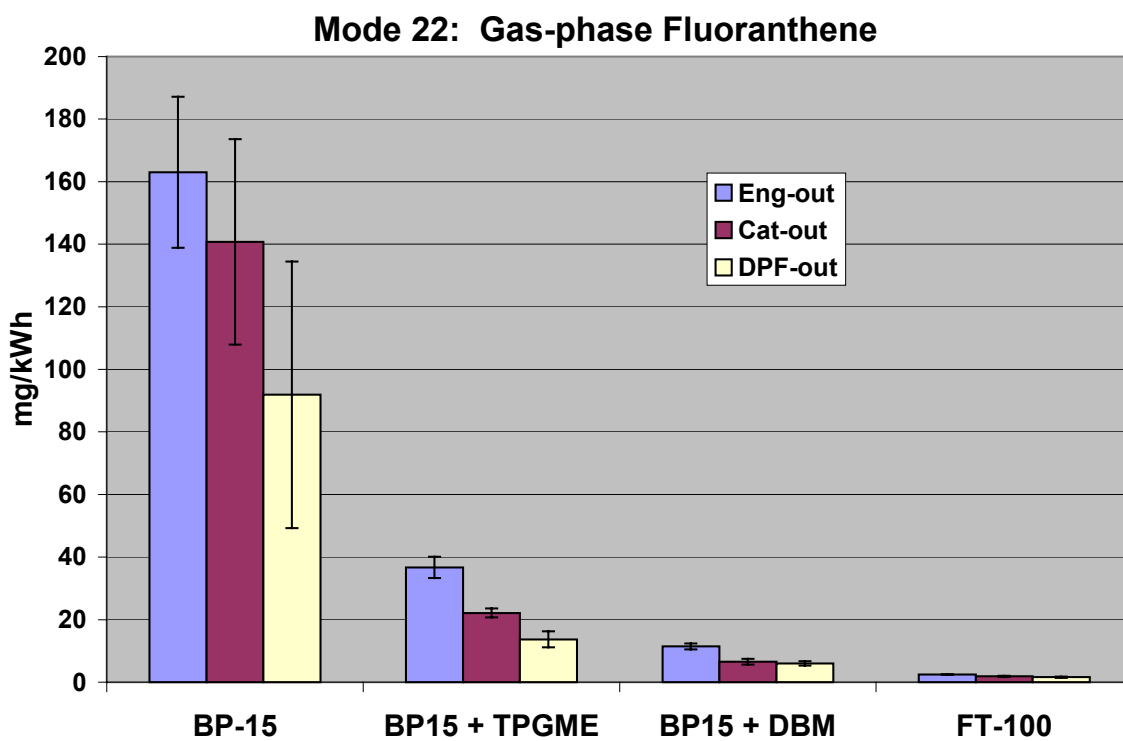


Figure D-18. Gas-Phase Fluoranthene Emissions by Fuel Type, Mode 22

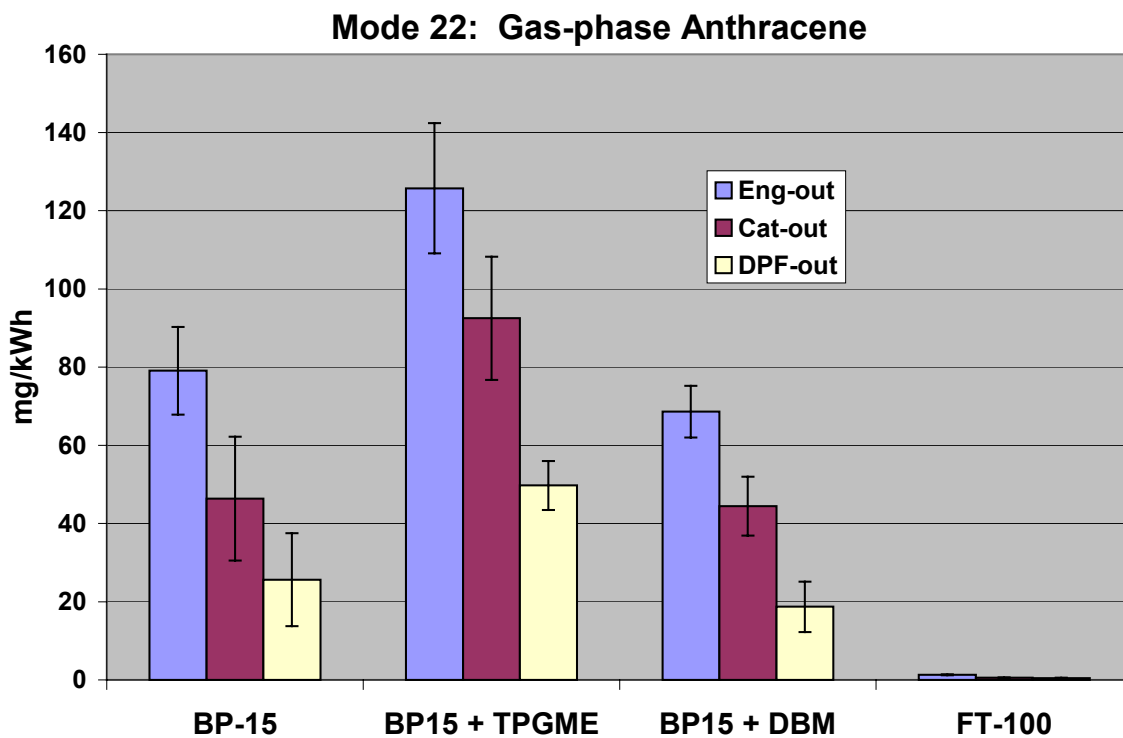


Figure D-19. Gas-Phase Anthracene Emissions by Fuel Type, Mode 22

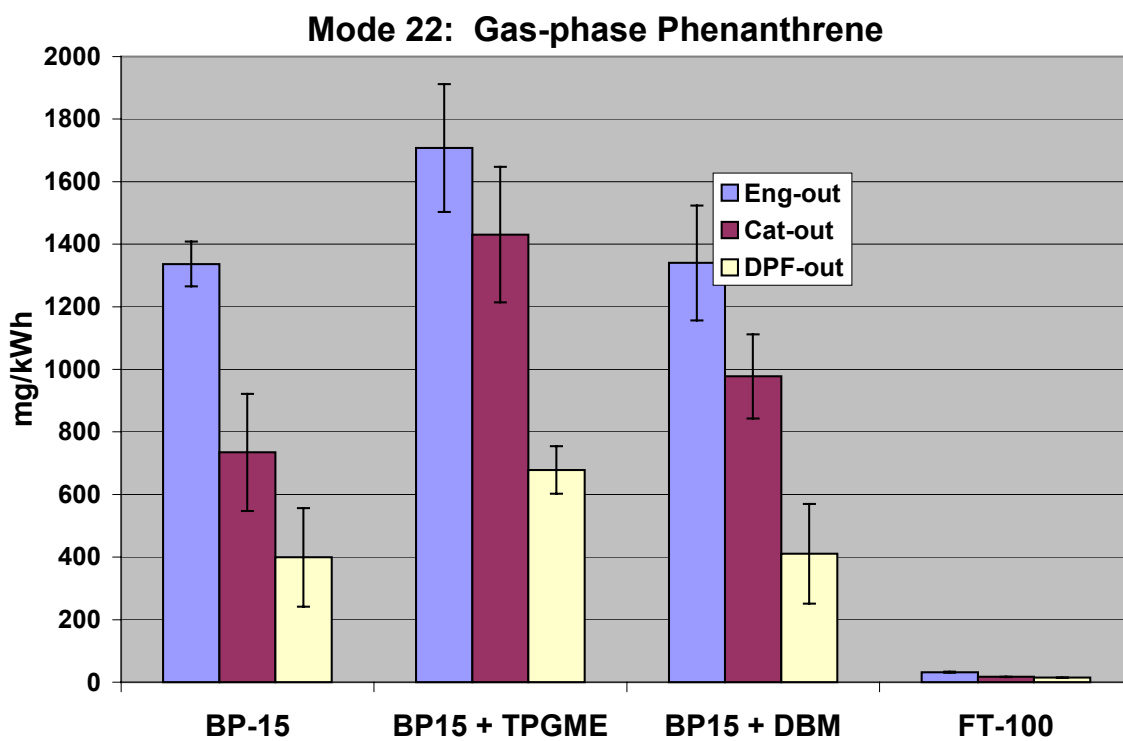


Figure D-20. Gas-Phase Phenanthrene Emissions by Fuel Type, Mode 22

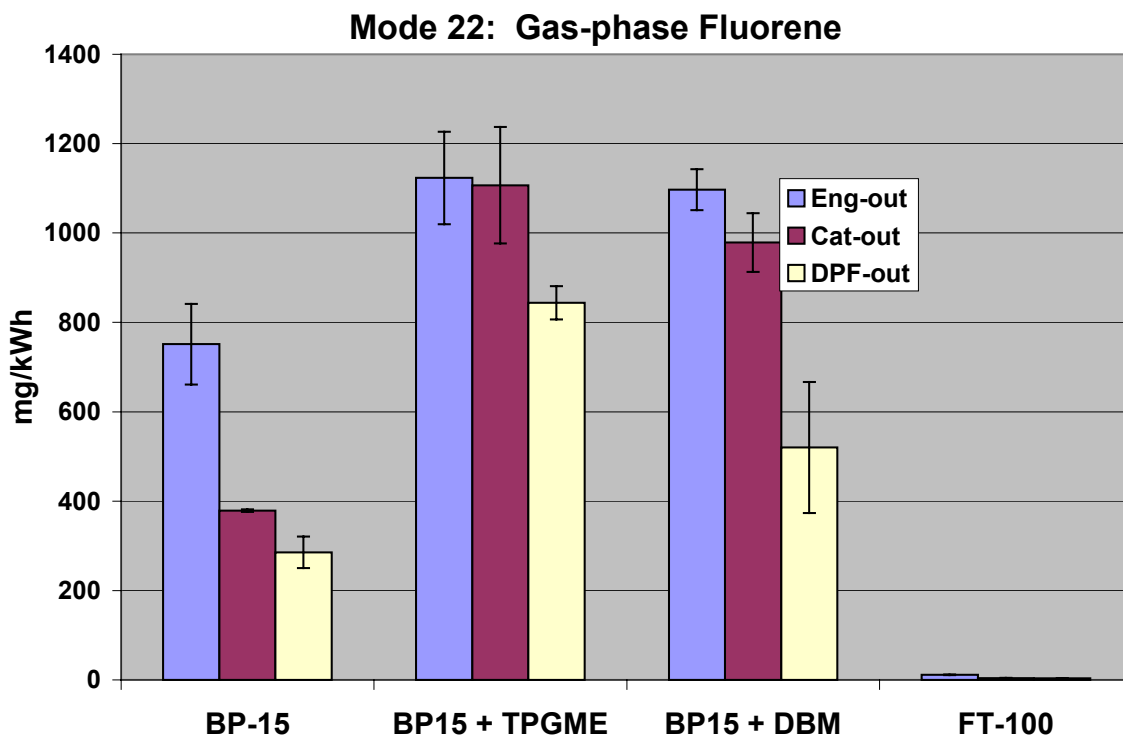


Figure D-21. Gas-Phase Fluorene Emissions by Fuel Type, Mode 22

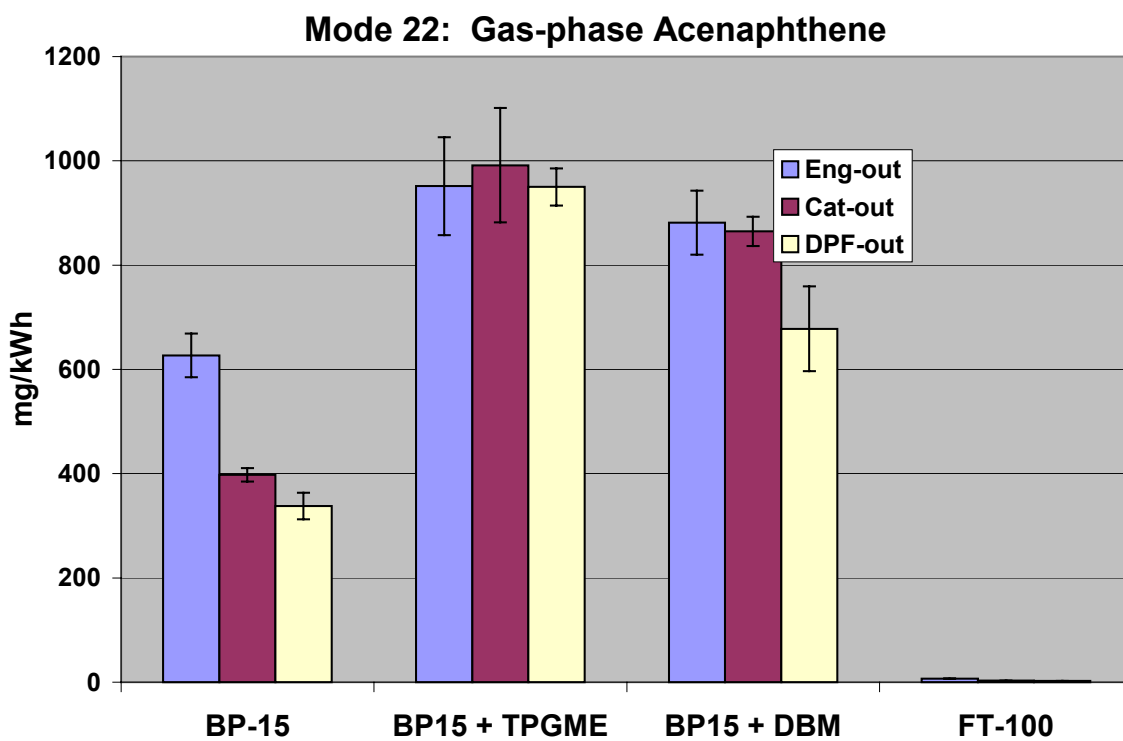


Figure D-22. Gas-Phase Acenaphthene Emissions by Fuel Type, Mode 22

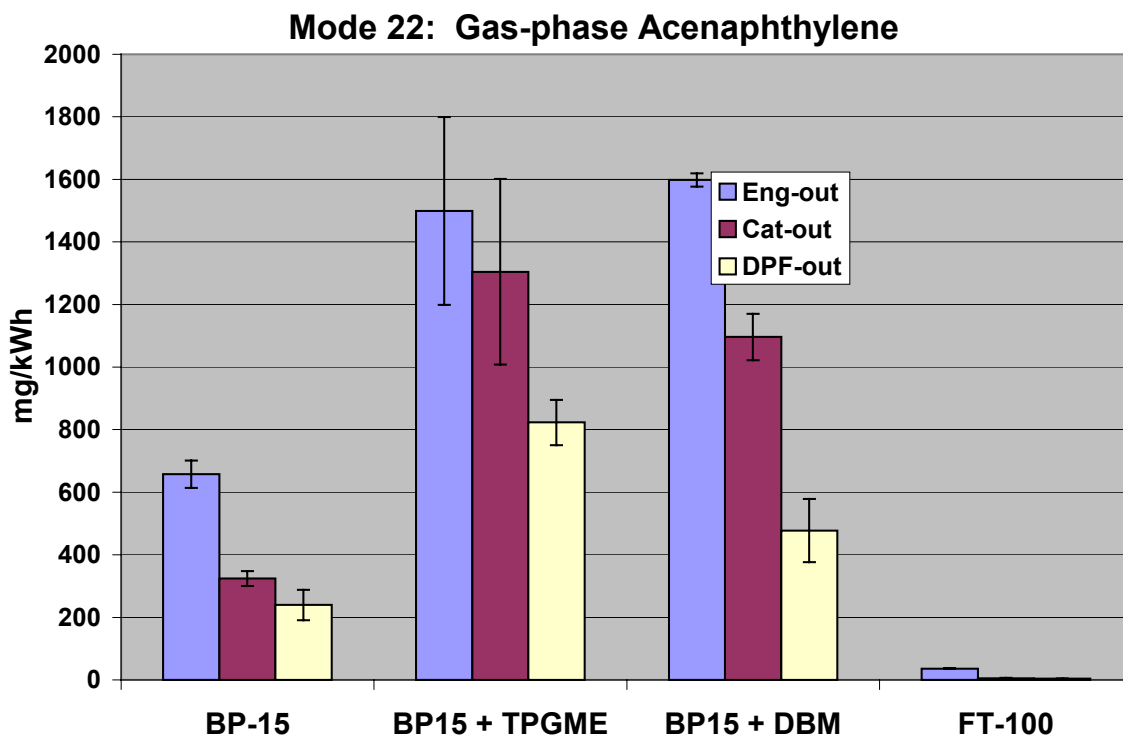


Figure D-23. Gas-Phase Acenaphthylene Emissions by Fuel Type, Mode 22

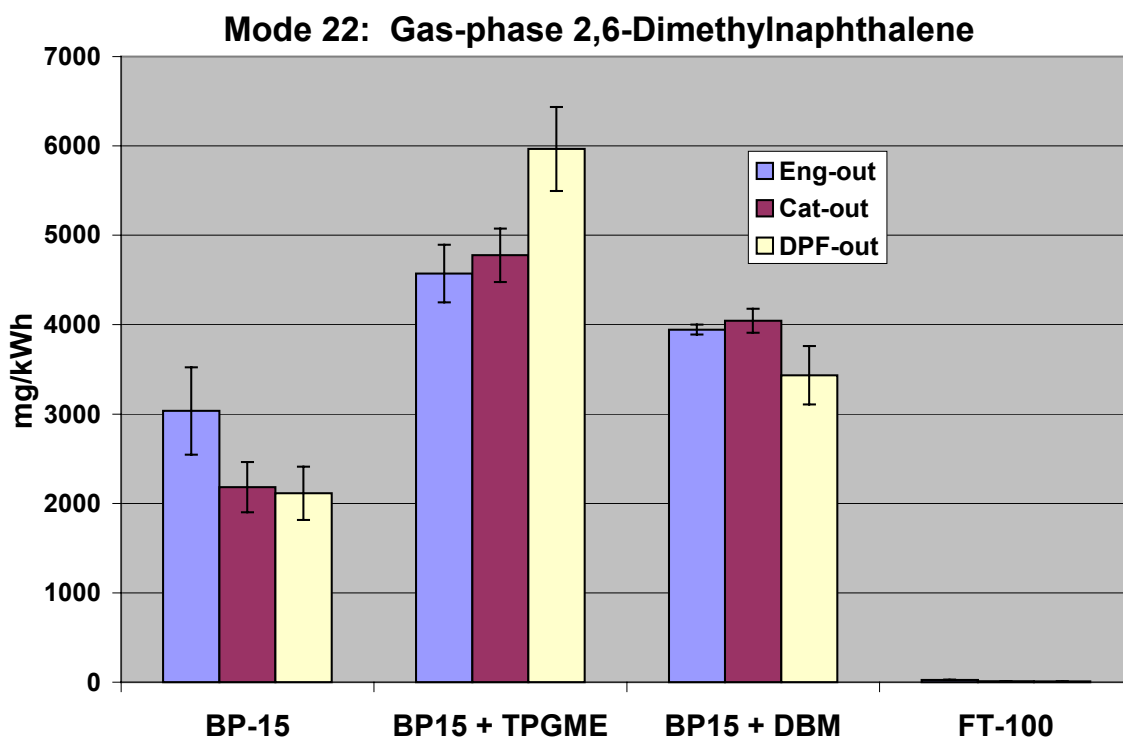


Figure D-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions by Fuel Type, Mode 22

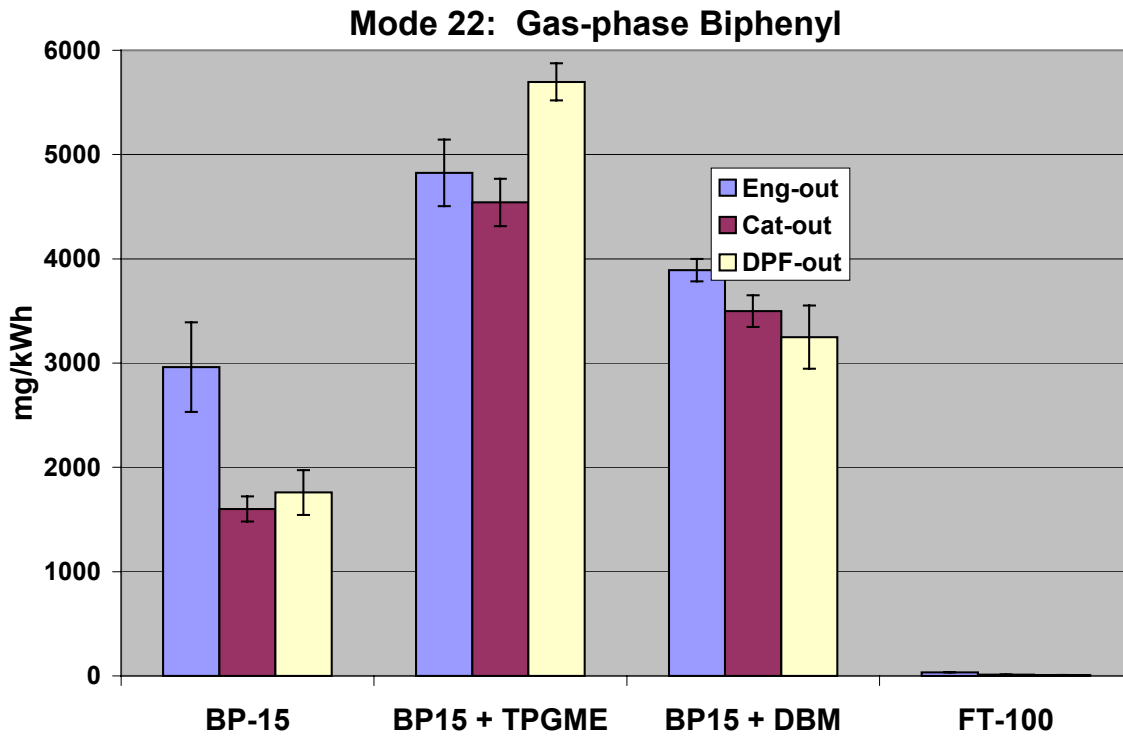


Figure D-25. Gas-Phase Biphenyl Emissions by Fuel Type, Mode 22

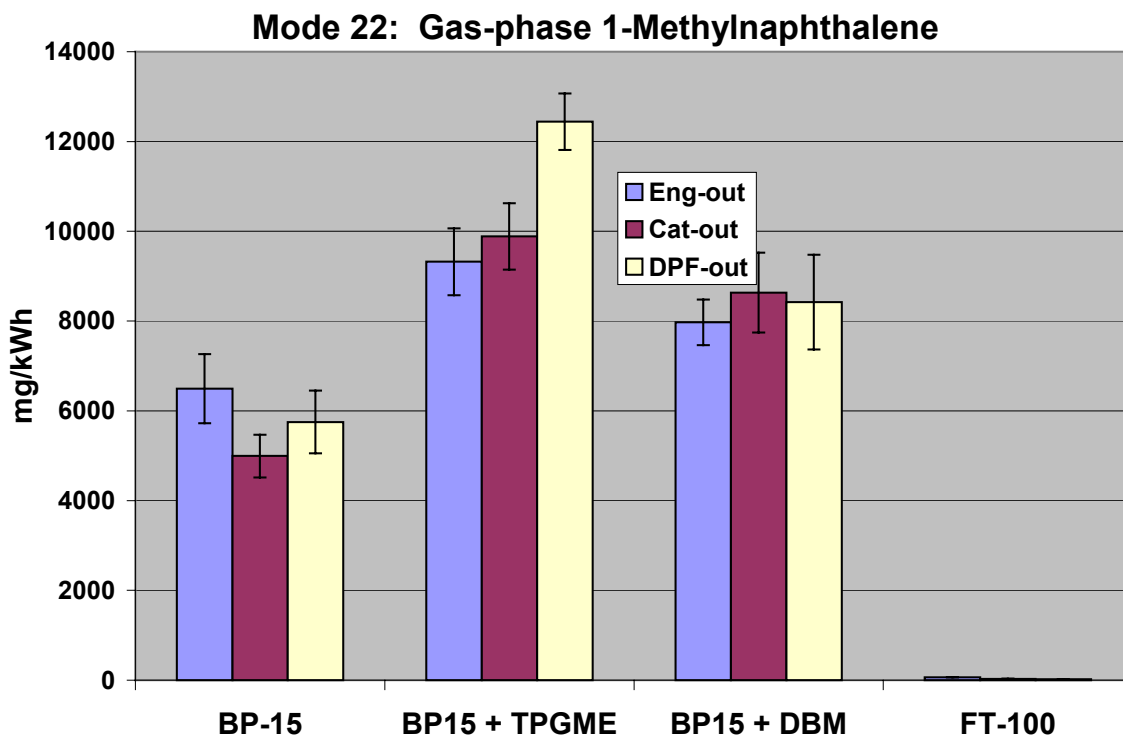


Figure D-26. Gas-Phase 1-Methylnaphthalene Emissions by Fuel Type, Mode 22

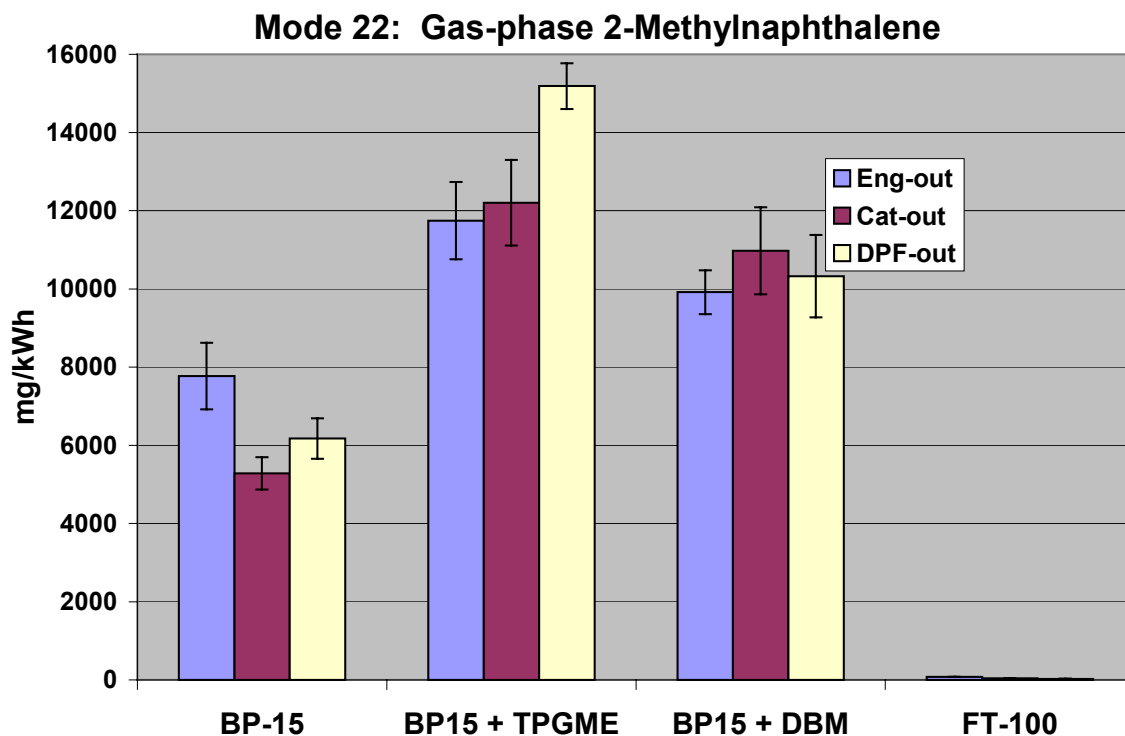


Figure D-27. Gas-Phase 2-Methylnaphthalene Emissions by Fuel Type, Mode 22

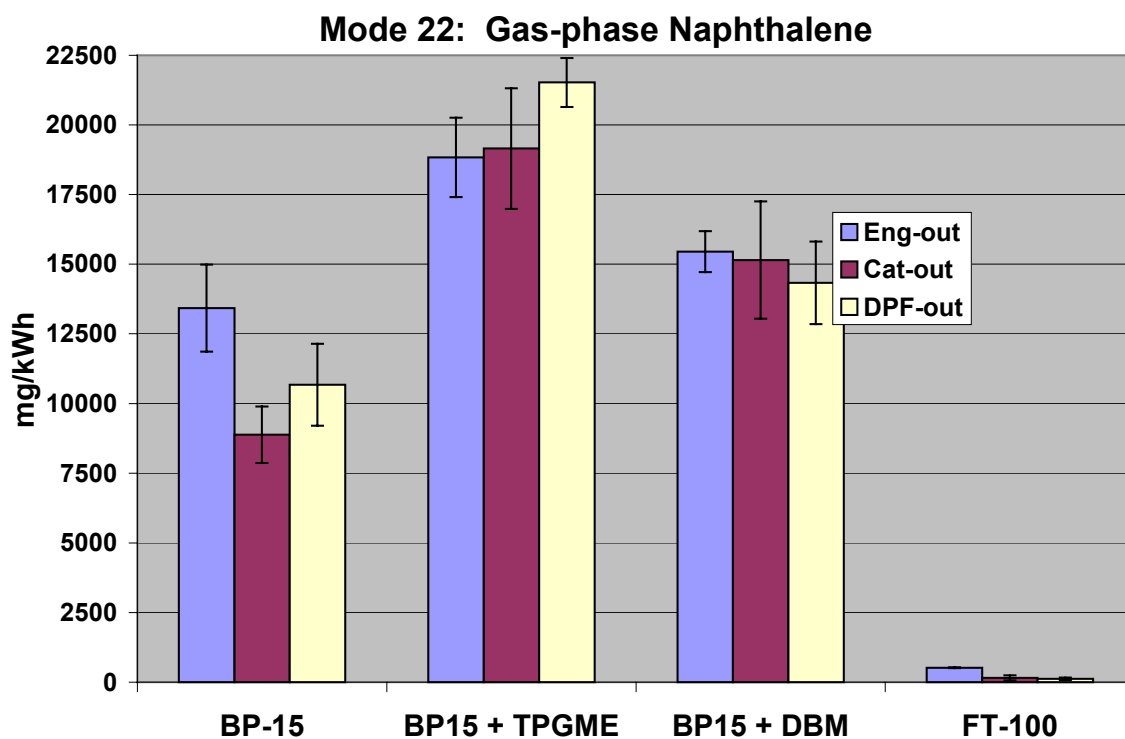


Figure D-28. Gas-Phase Naphthalene Emissions by Fuel Type, Mode 22

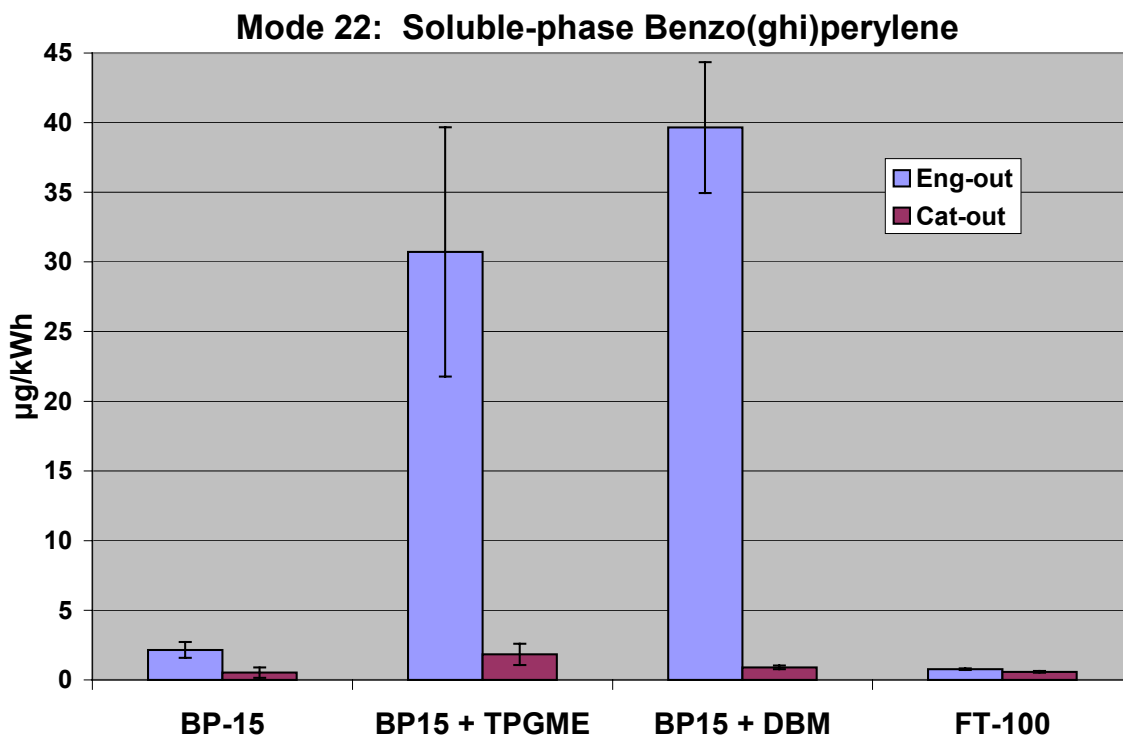


Figure D-29. Soluble-Phase Benzo(ghi)perylene Emissions by Fuel Type, Mode 22

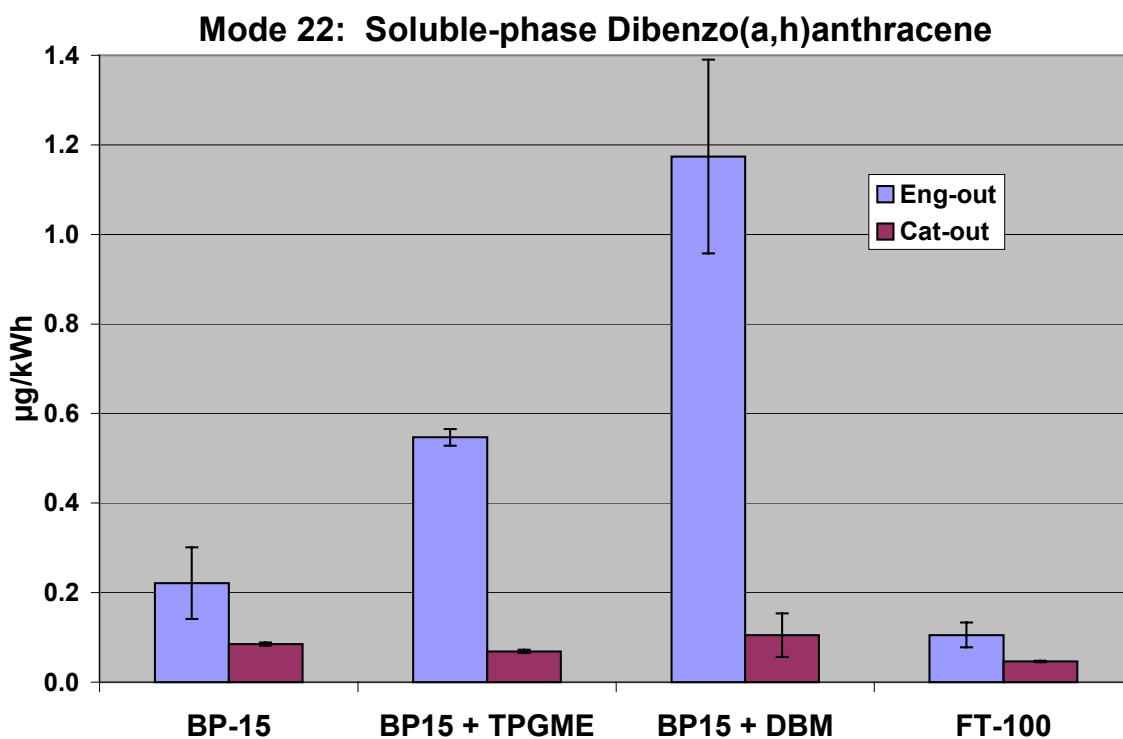


Figure D-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions by Fuel Type, Mode 22

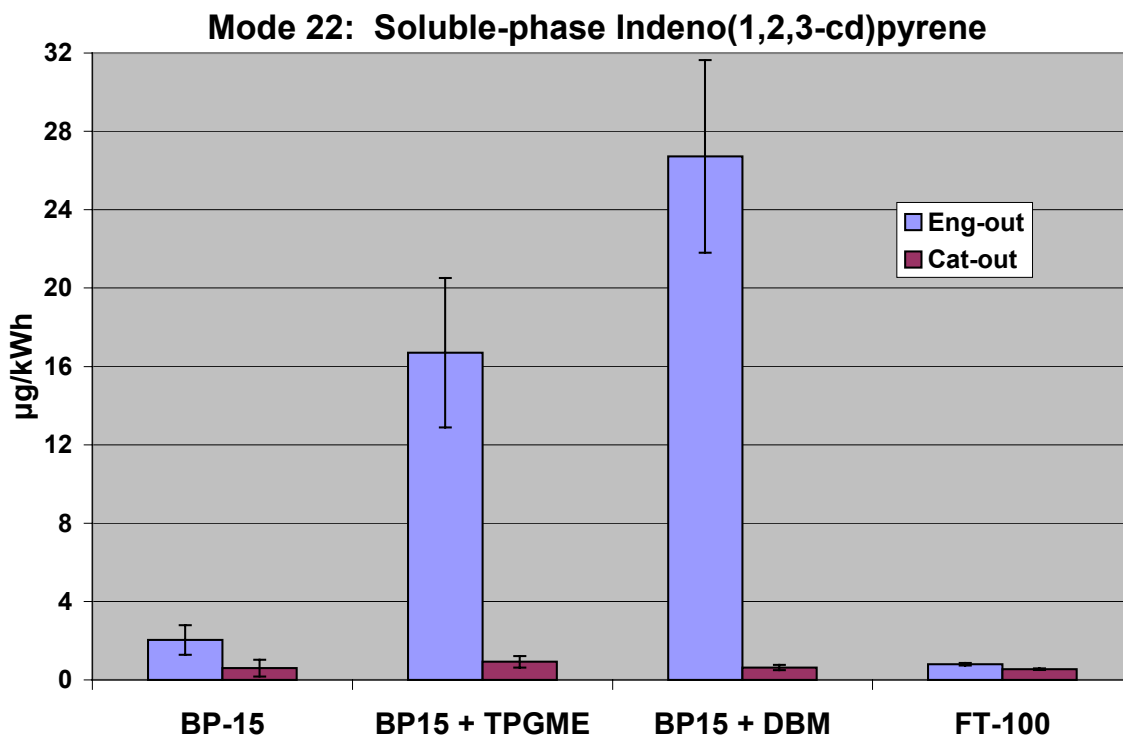


Figure D-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions by Fuel Type, Mode 22

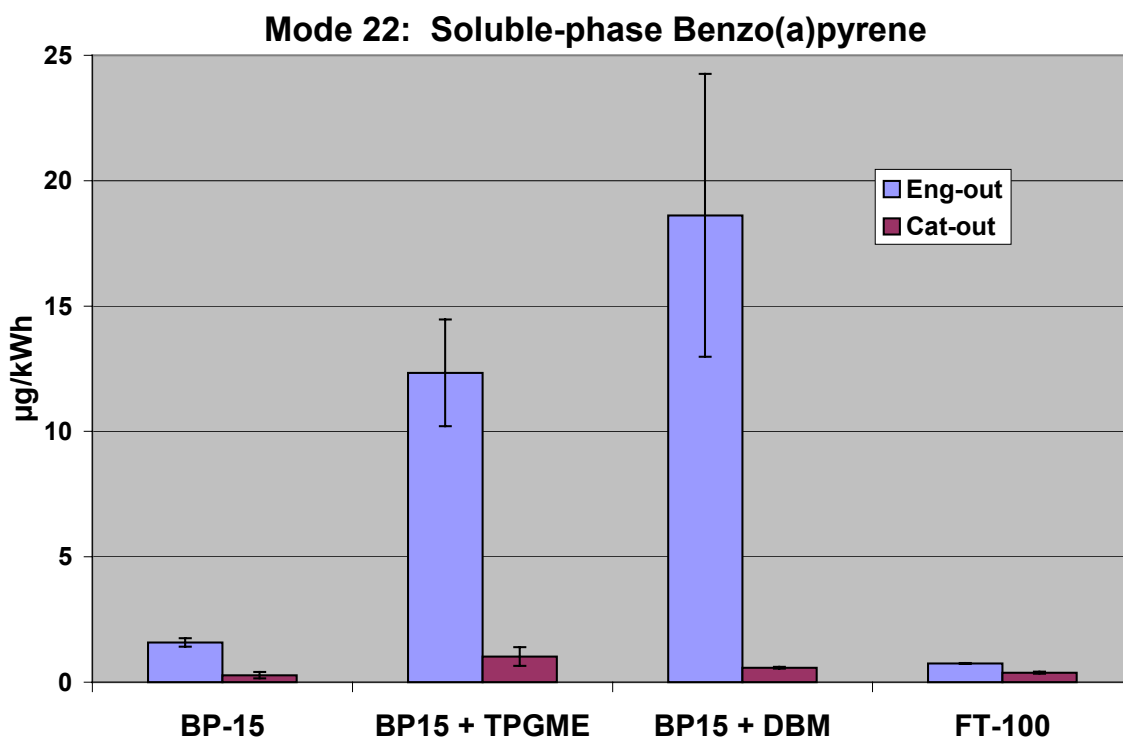


Figure D-32. Soluble-Phase Benzo(a)pyrene Emissions by Fuel Type, Mode 22



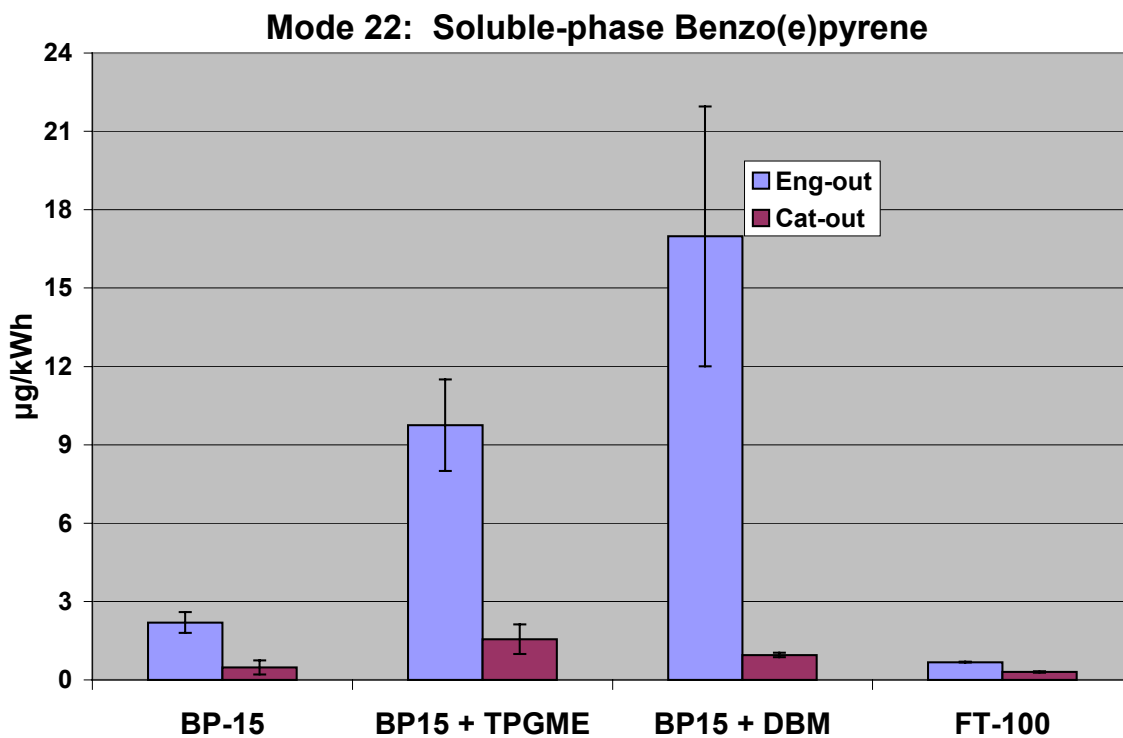


Figure D-33. Soluble-Phase Benzo(e)pyrene Emissions by Fuel Type, Mode 22

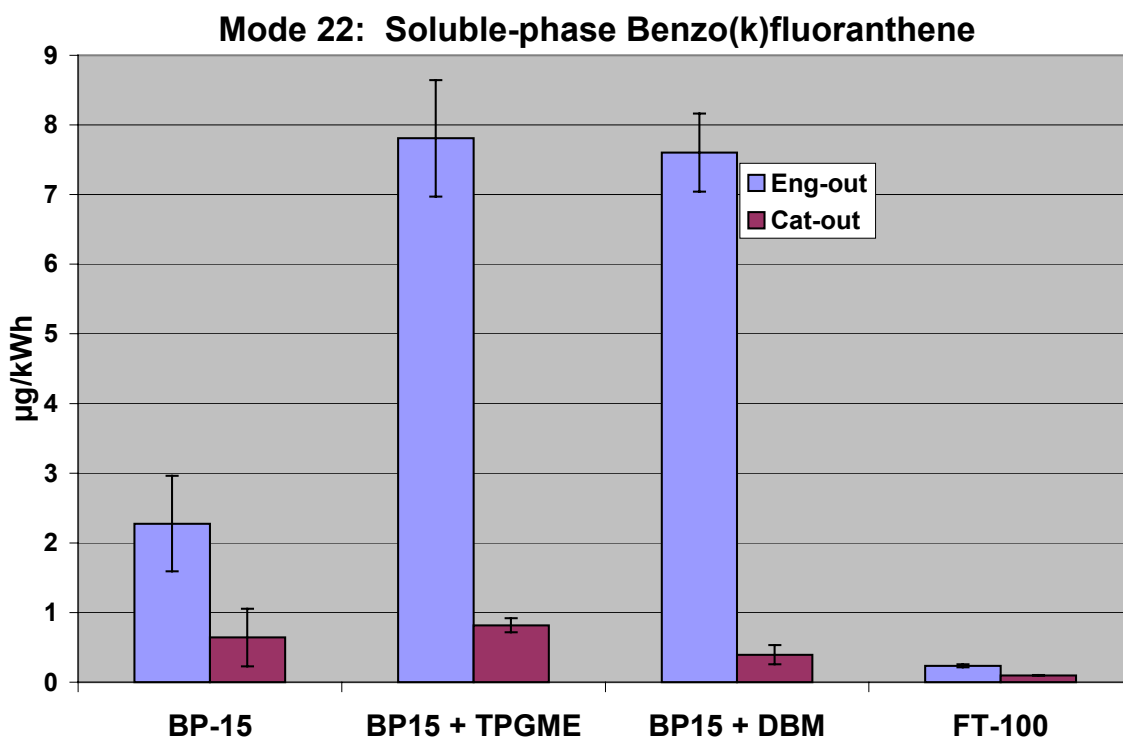


Figure D-34. Soluble-Phase Benzo(k)fluoranthene Emissions by Fuel Type, Mode 22

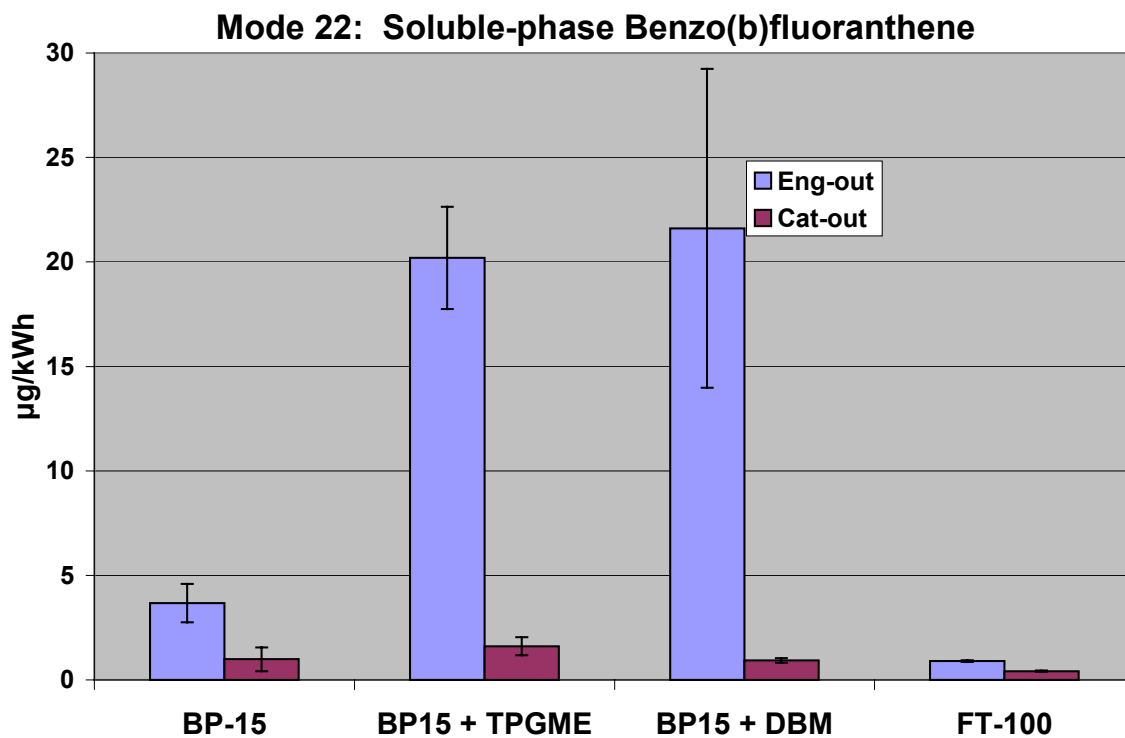


Figure D-35. Soluble-Phase Benzo(b)fluoranthene Emissions by Fuel Type, Mode 22

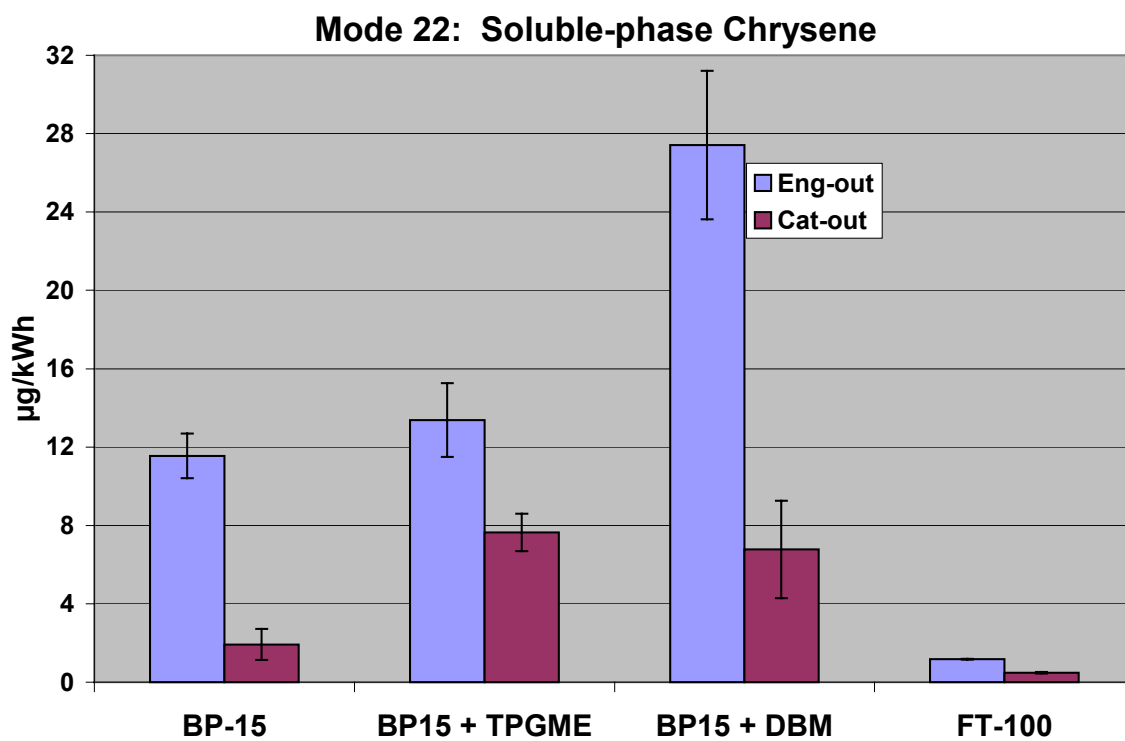


Figure D-36. Soluble-Phase Chrysene Emissions by Fuel Type, Mode 22

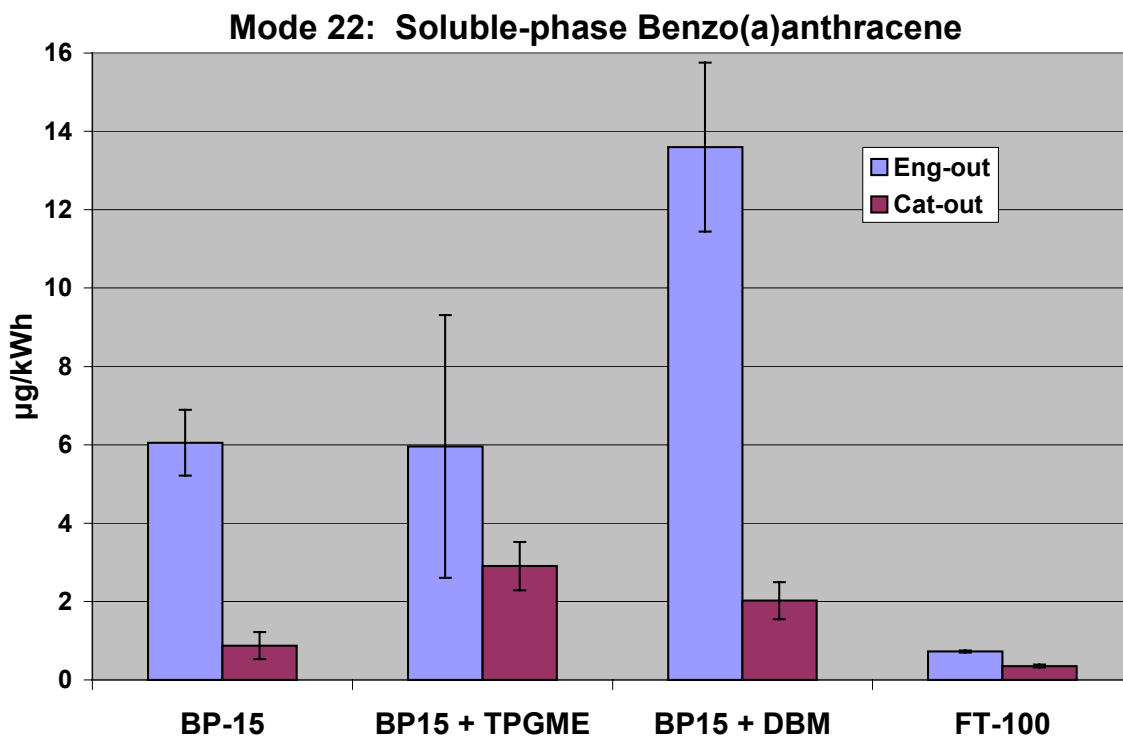


Figure D-37. Soluble-Phase Benzo(a)anthracene Emissions by Fuel Type, Mode 22

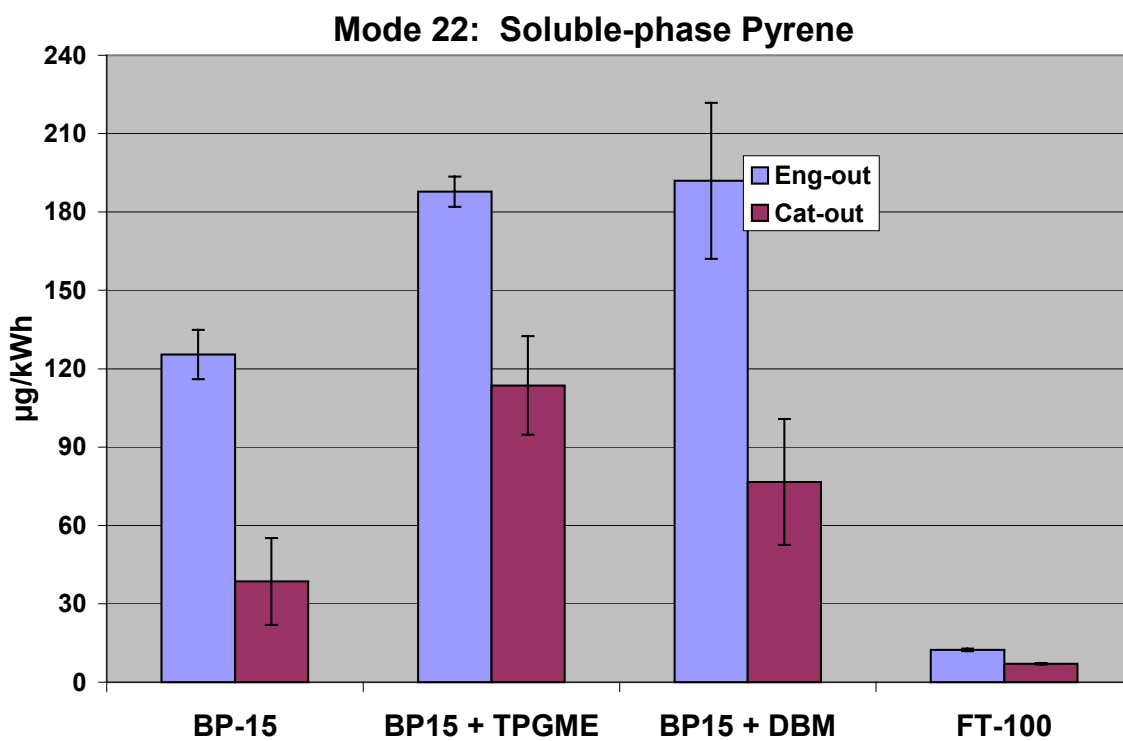


Figure D-38. Soluble-Phase Pyrene Emissions by Fuel Type, Mode 22

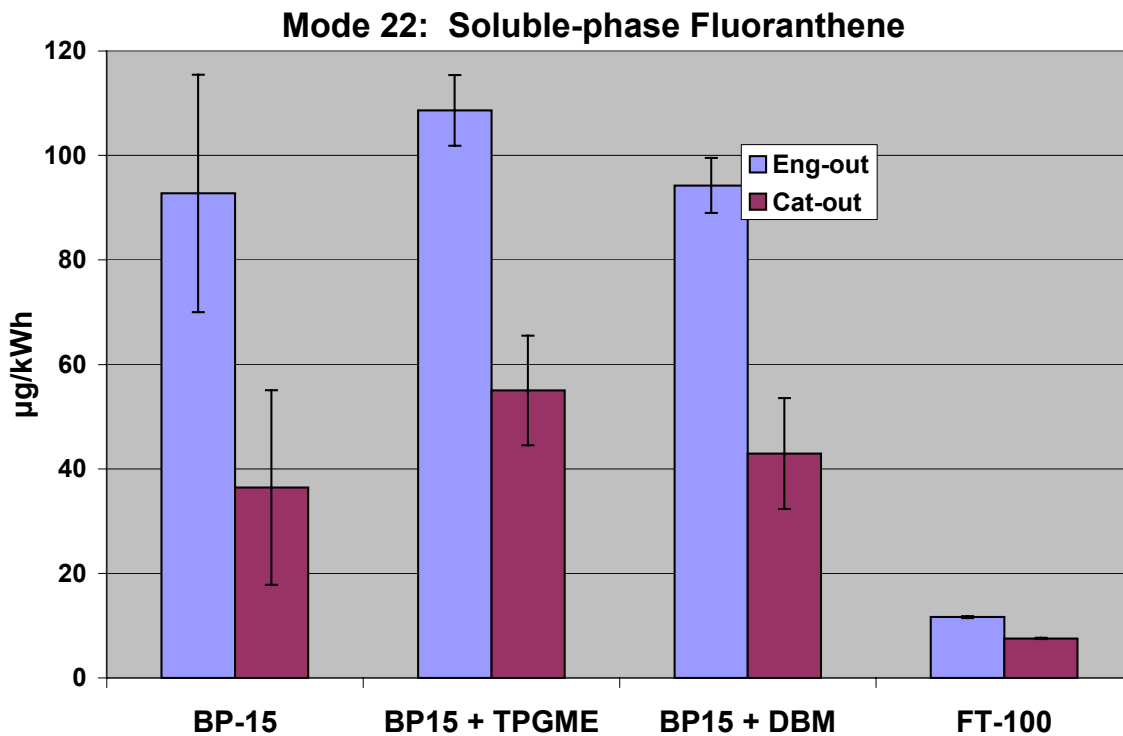


Figure D-39. Soluble-Phase Fluoranthene Emissions by Fuel Type, Mode 22

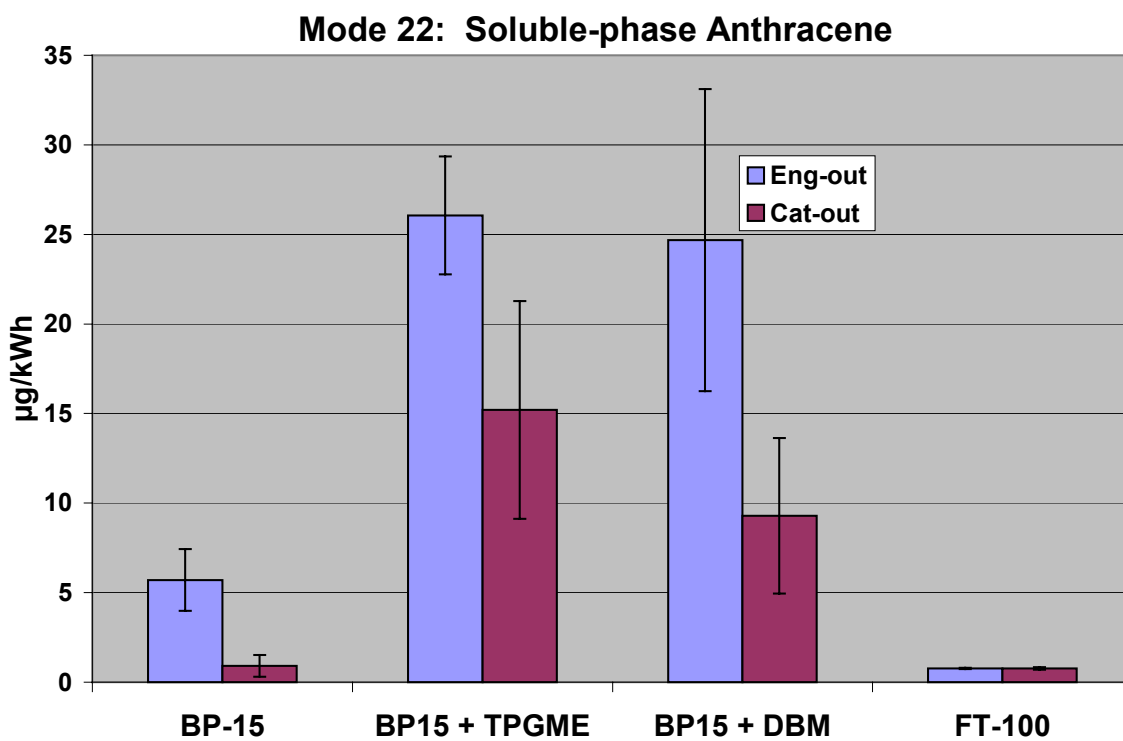


Figure D-40. Soluble-Phase Anthracene Emissions by Fuel Type, Mode 22

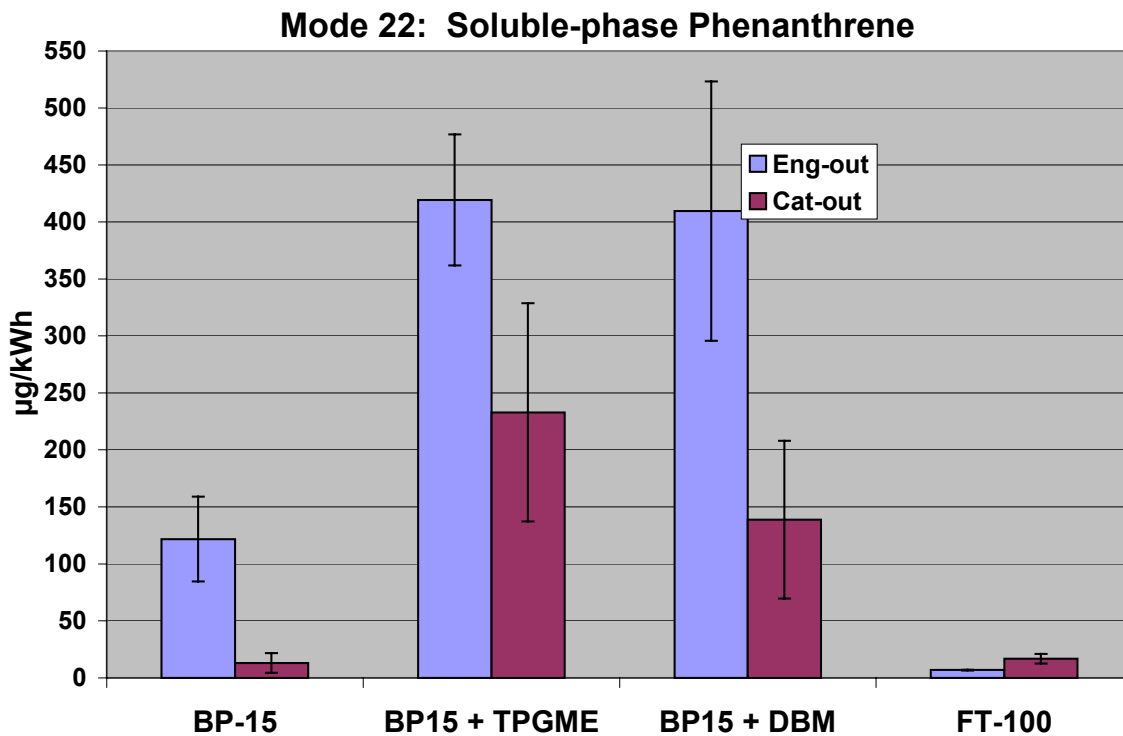


Figure D-41. Soluble-Phase Phenanthrene Emissions by Fuel Type, Mode 22

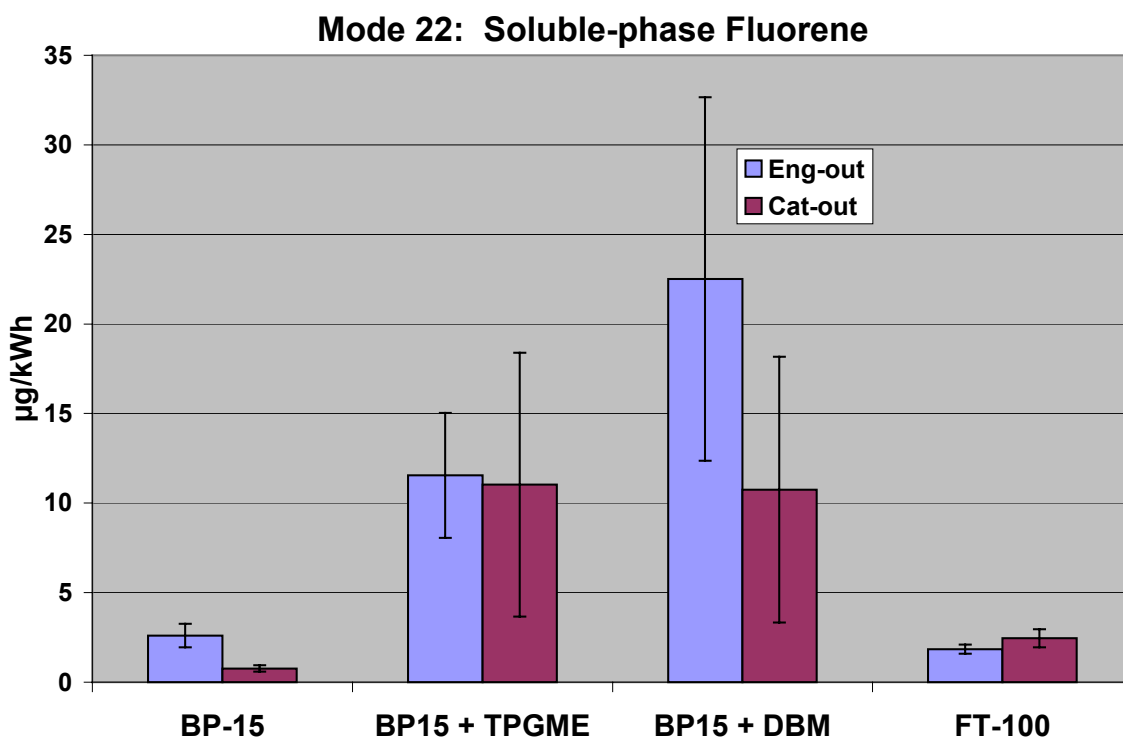


Figure D-42. Soluble-Phase Fluorene Emissions by Fuel Type, Mode 22

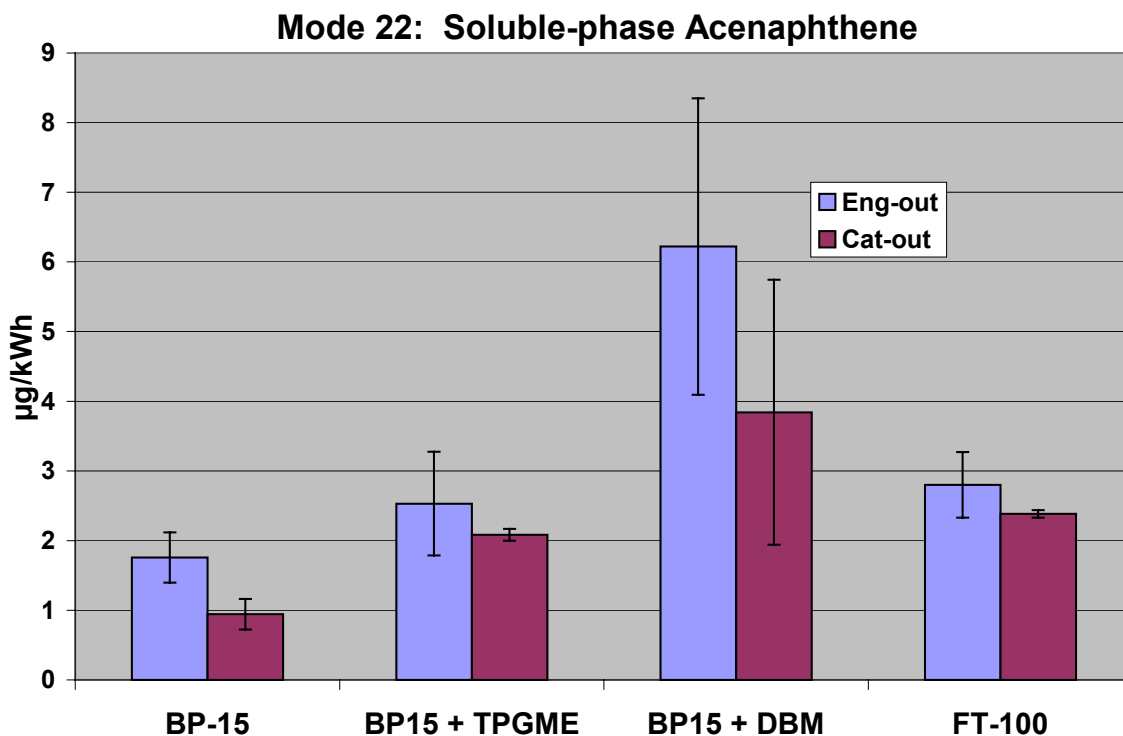


Figure D-43. Soluble-Phase Acenaphthene Emissions by Fuel Type, Mode 22

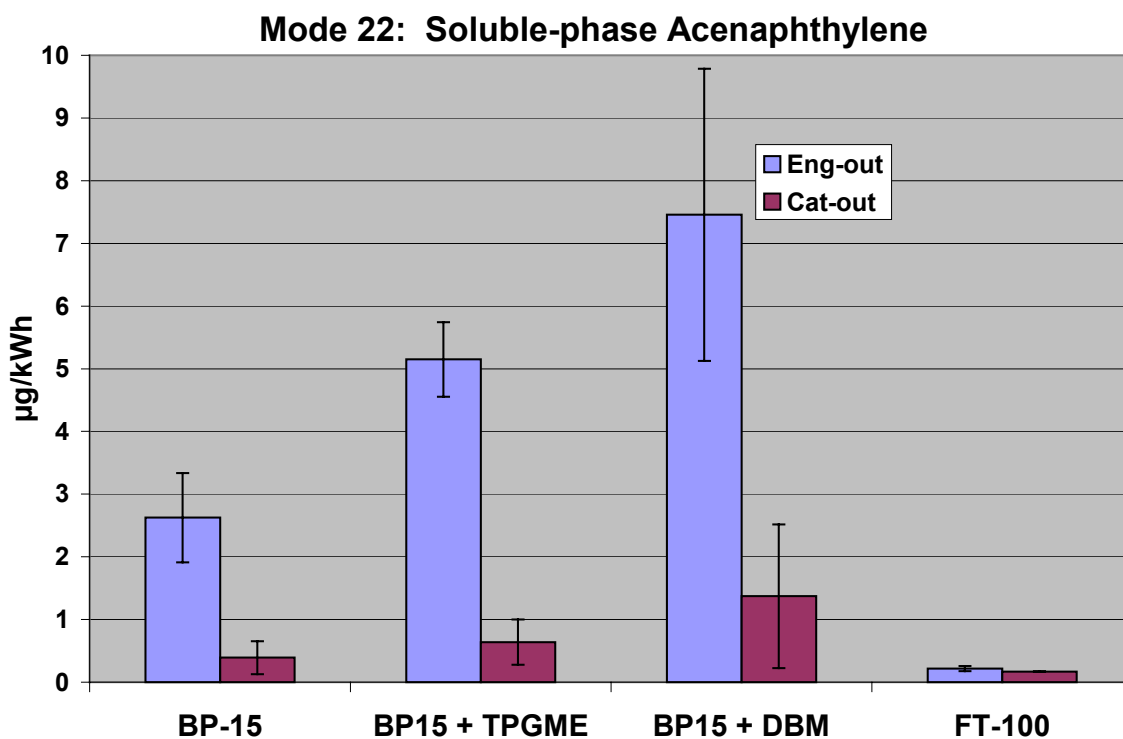


Figure D-44. Soluble-Phase Acenaphthylene Emissions by Fuel Type, Mode 22

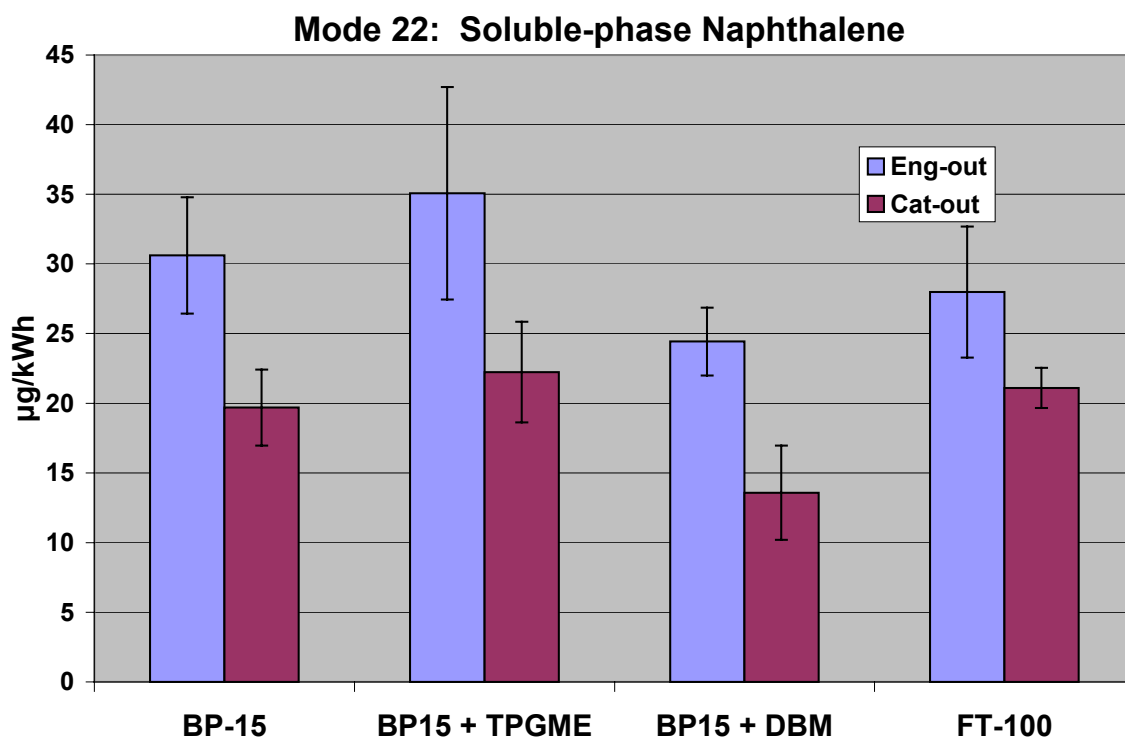


Figure D-45. Soluble-Phase Naphthalene Emissions by Fuel Type, Mode 22

## **APPENDIX E**

### **BP15 Fuel Operation Test Results**



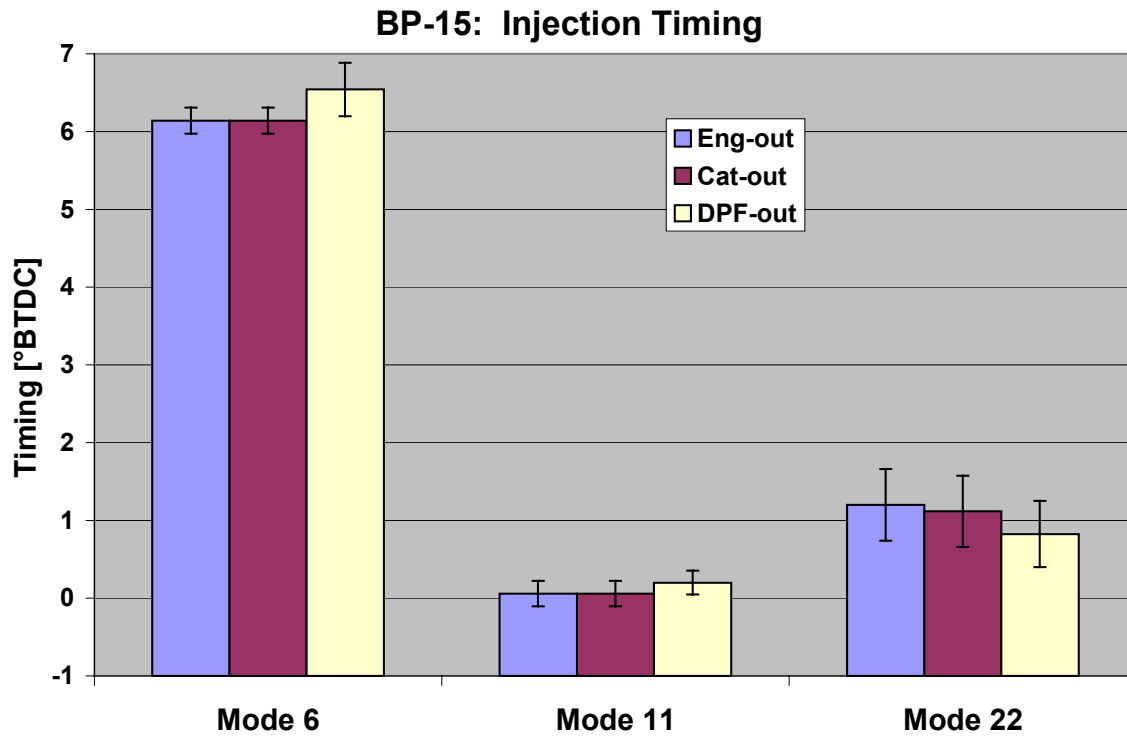


Figure E-1. Injection Timing with BP-15 Fuel

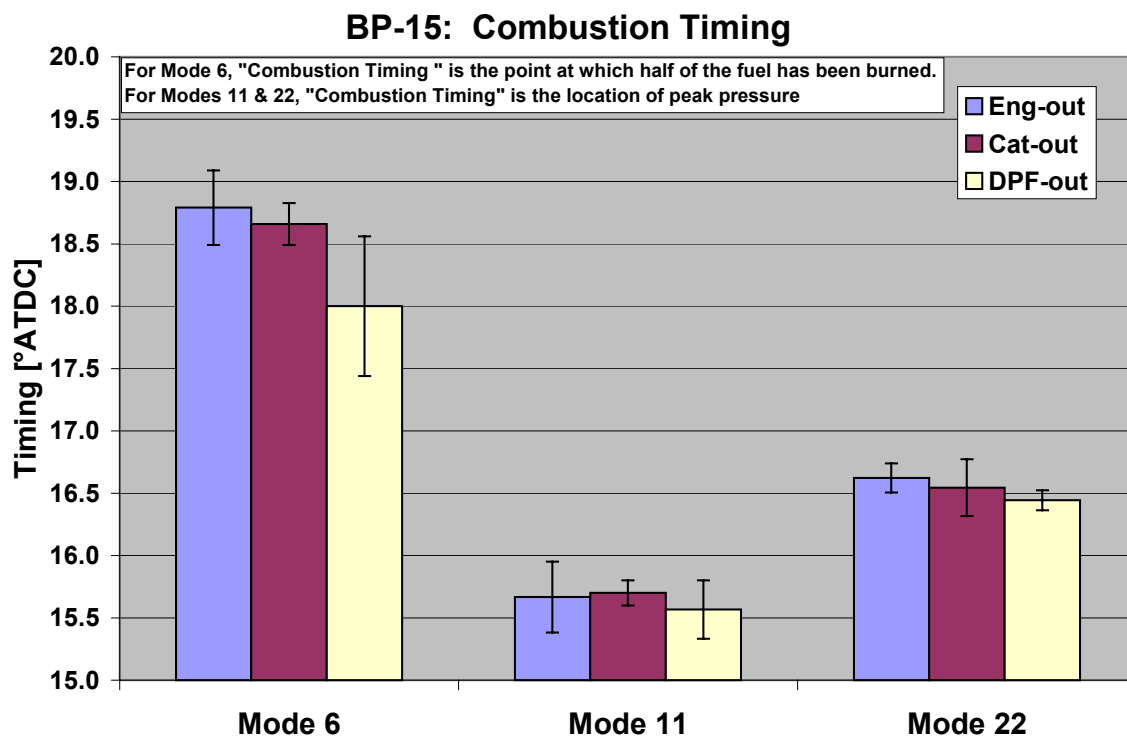


Figure E-2. Combustion Timing with BP-15 Fuel

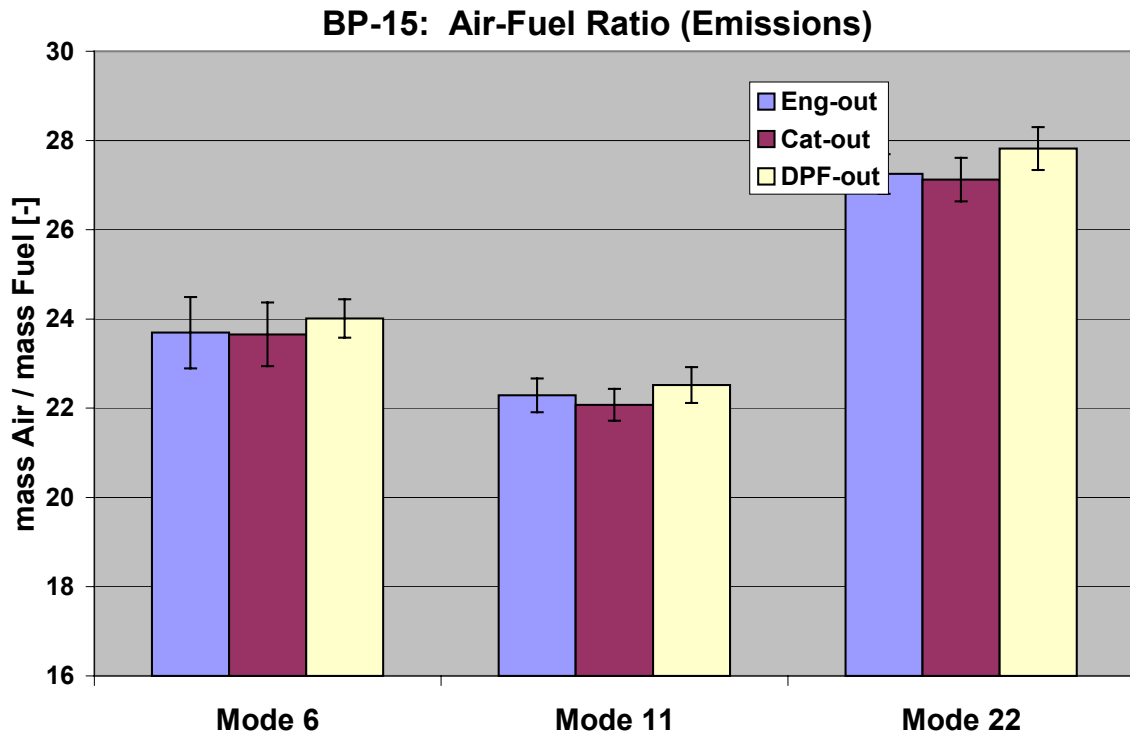


Figure E-3. Emissions Air-Fuel Ratio with BP-15 Fuel

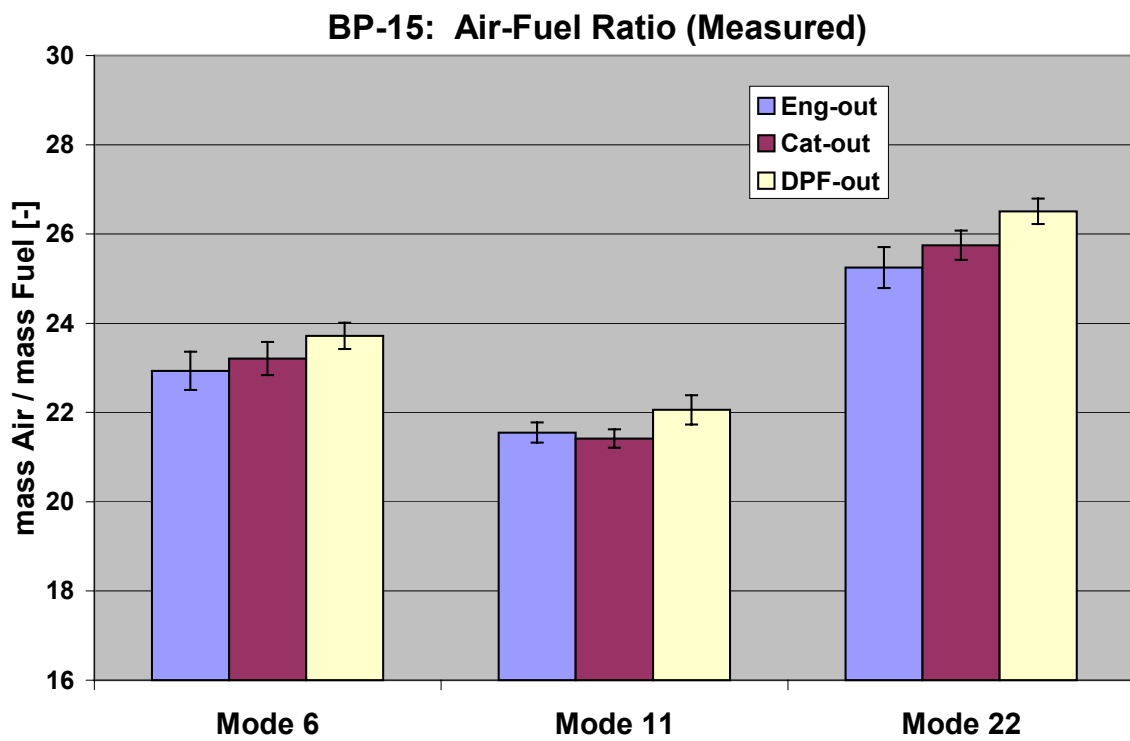


Figure E-4. Measured Air-Fuel Ratio with BP-15 Fuel

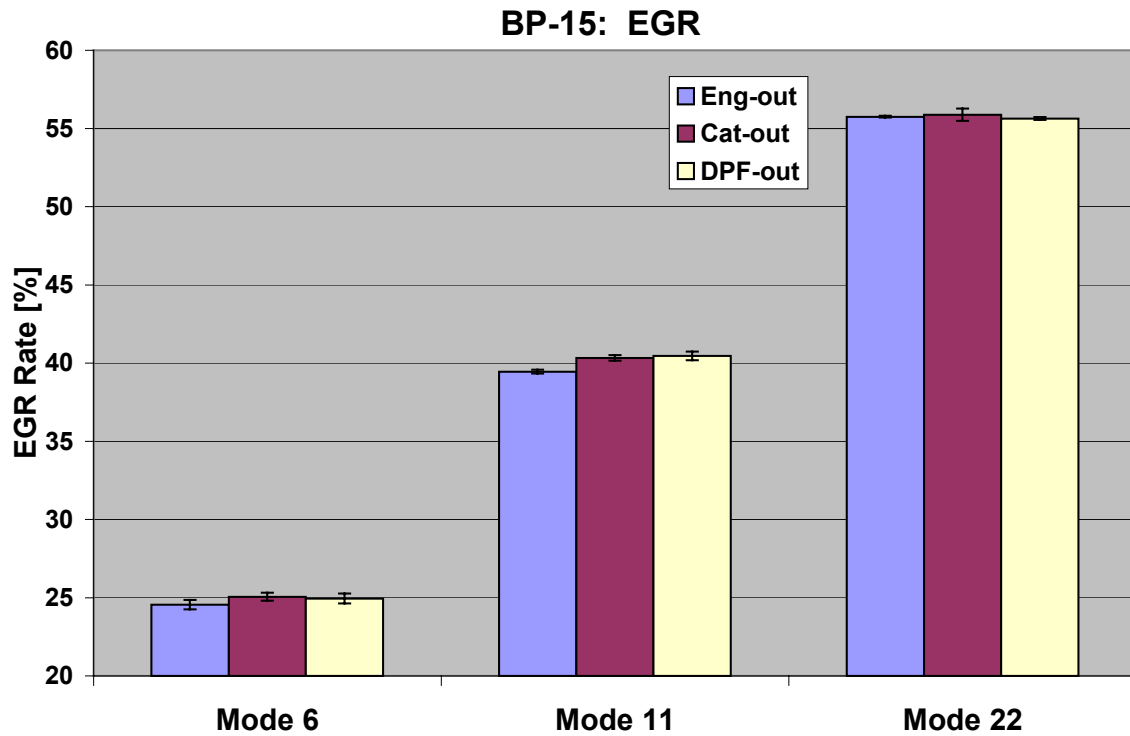


Figure E-5. EGR Rate with BP-15 Fuel

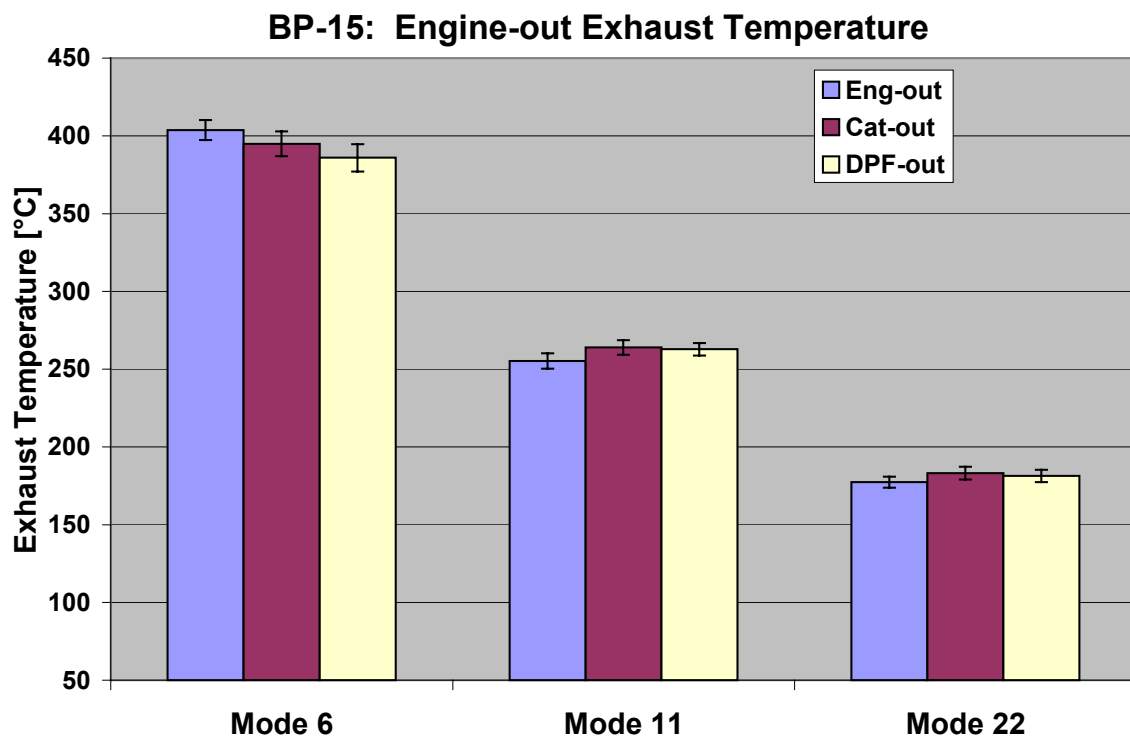


Figure E-6. Engine-Out Exhaust Temperature with BP-15 Fuel

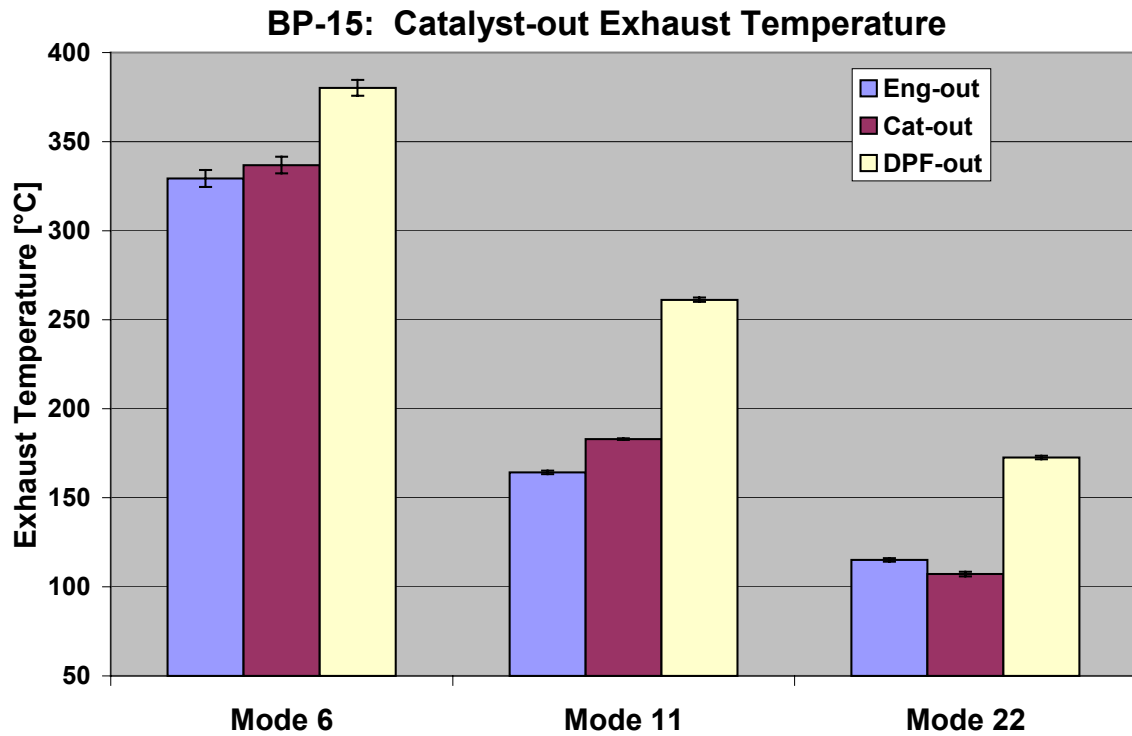


Figure E-7. Catalyst-Out Exhaust Temperature with BP-15 Fuel

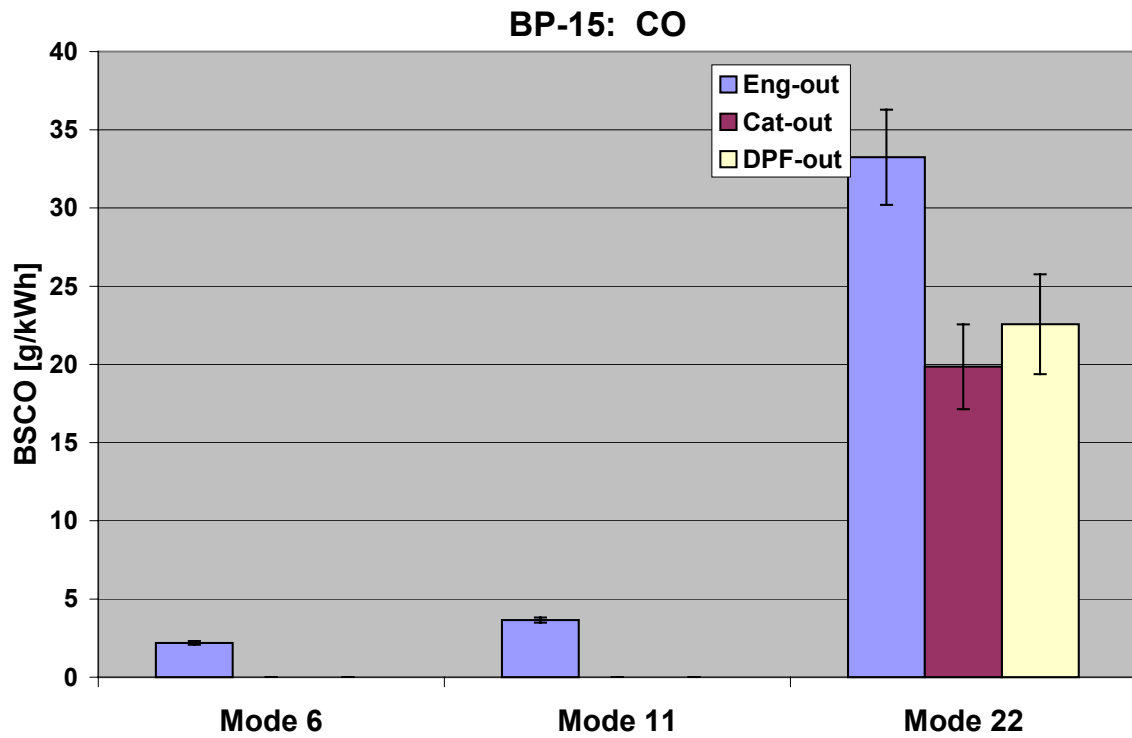


Figure E-8. Carbon Monoxide Emissions with BP-15 Fuel

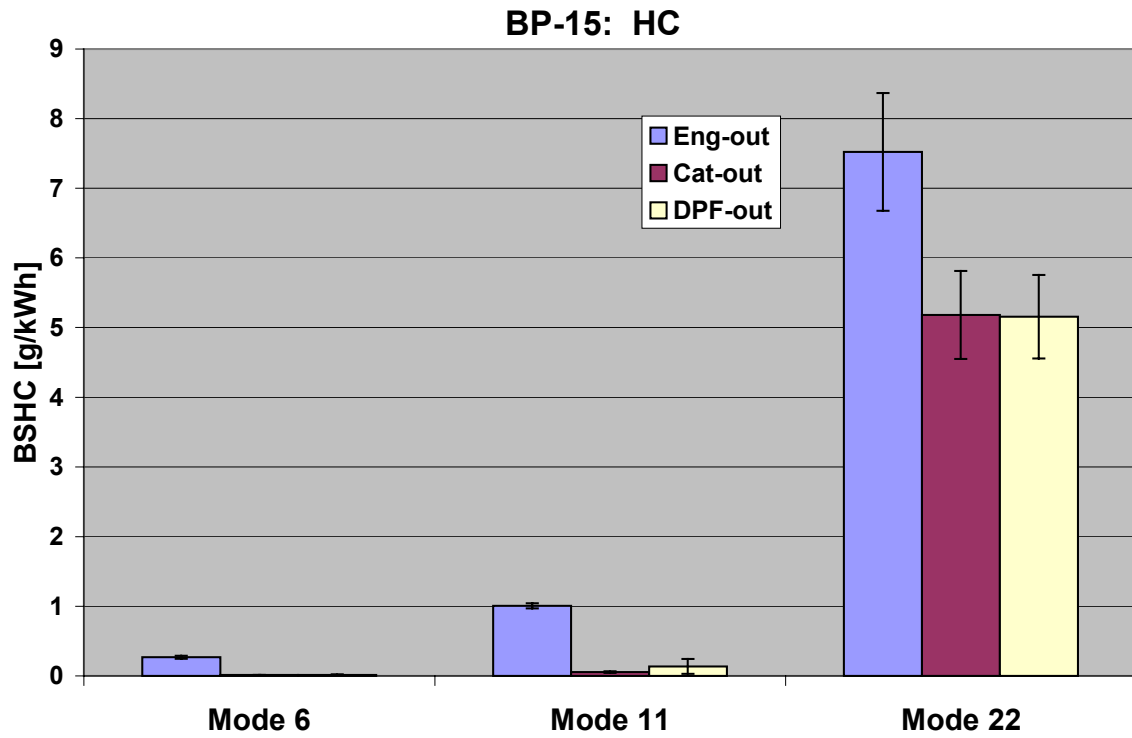


Figure E-9. Hydrocarbon Emissions with BP-15 Fuel

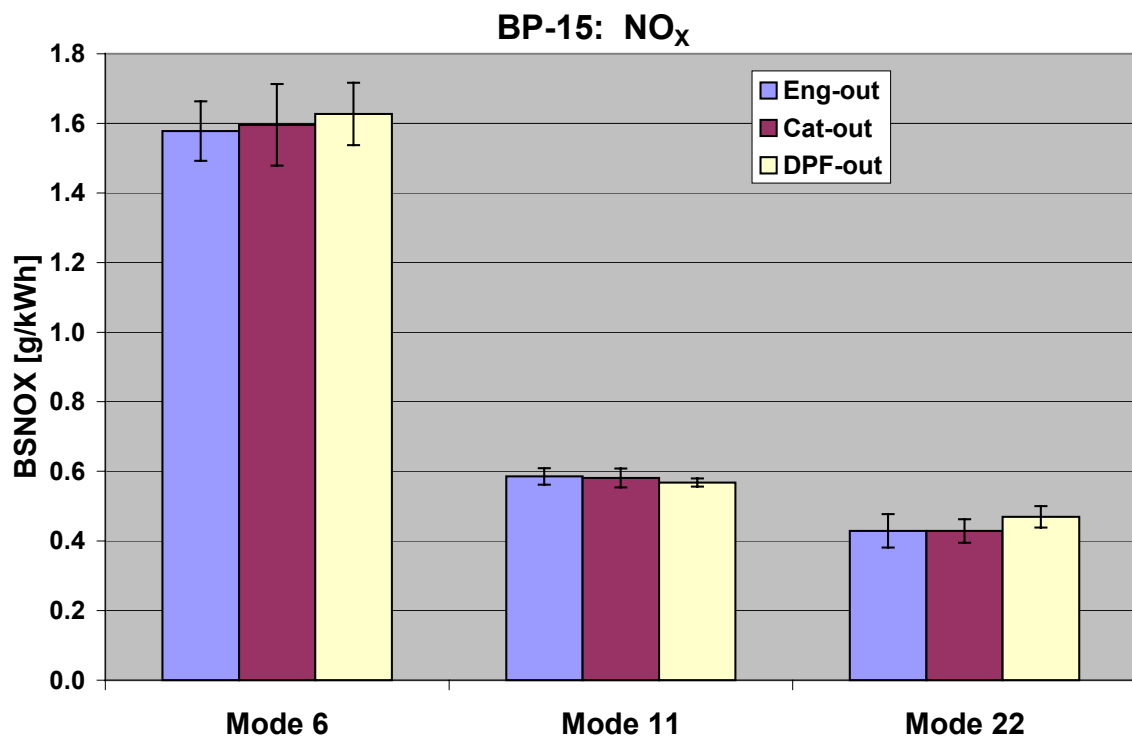


Figure E-10. Nitrogen Oxides Emissions with BP-15 Fuel

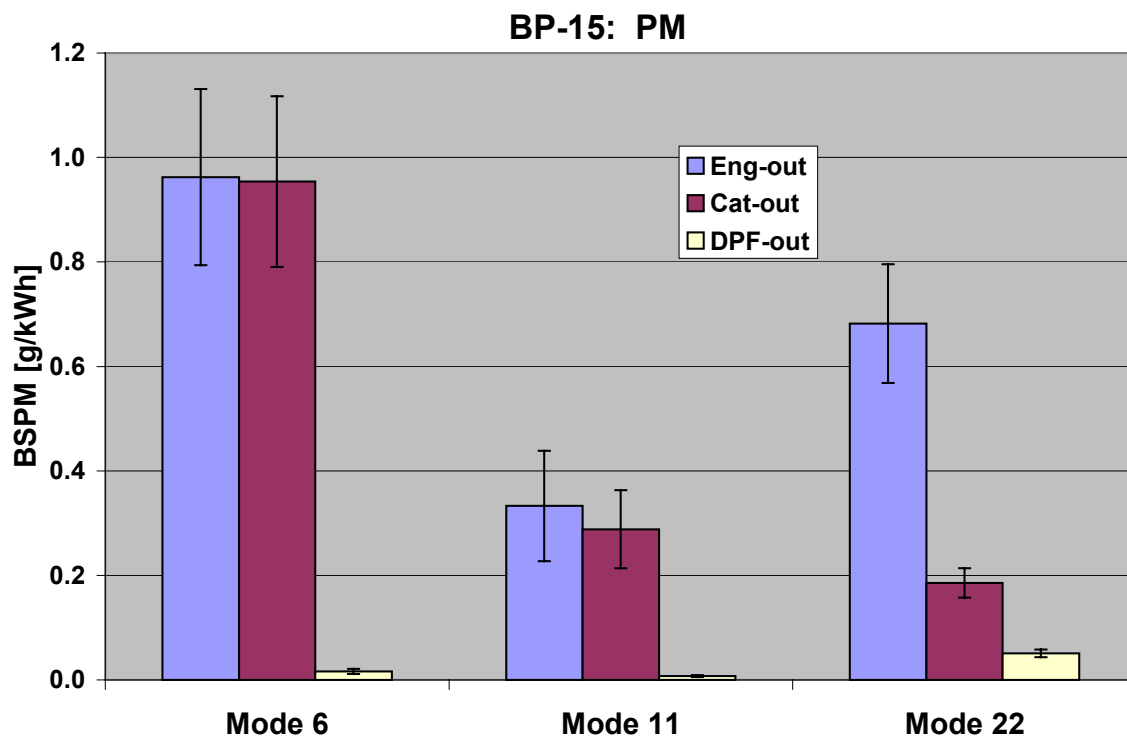


Figure E-11. Particulate Matter Emissions with BP-15 Fuel

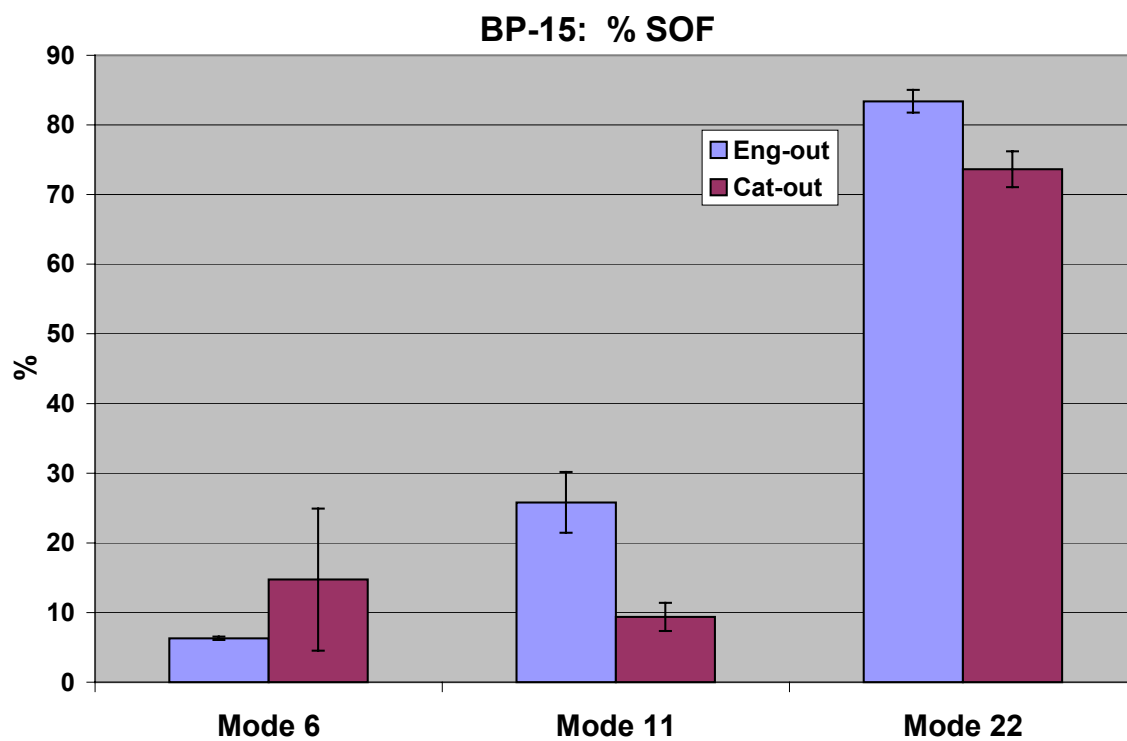


Figure E-12. Percent Soluble Organic Fraction with BP-15 Fuel

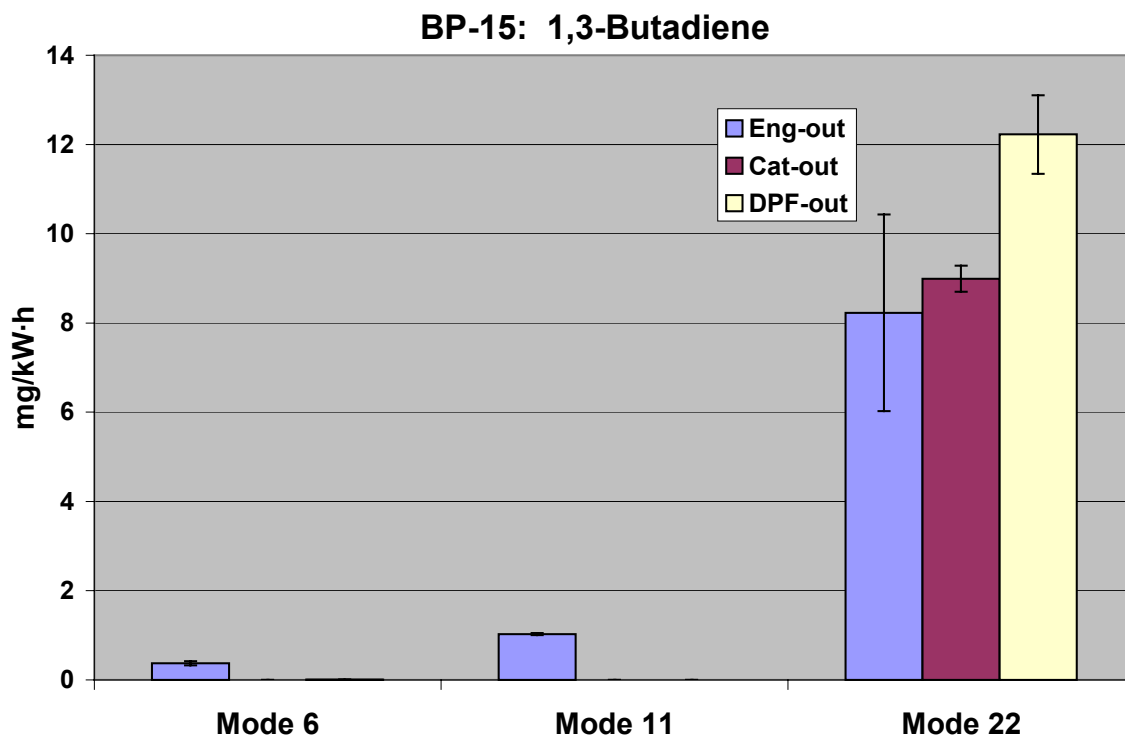


Figure E-13. 1,3-Butadiene Emissions with BP-15 Fuel

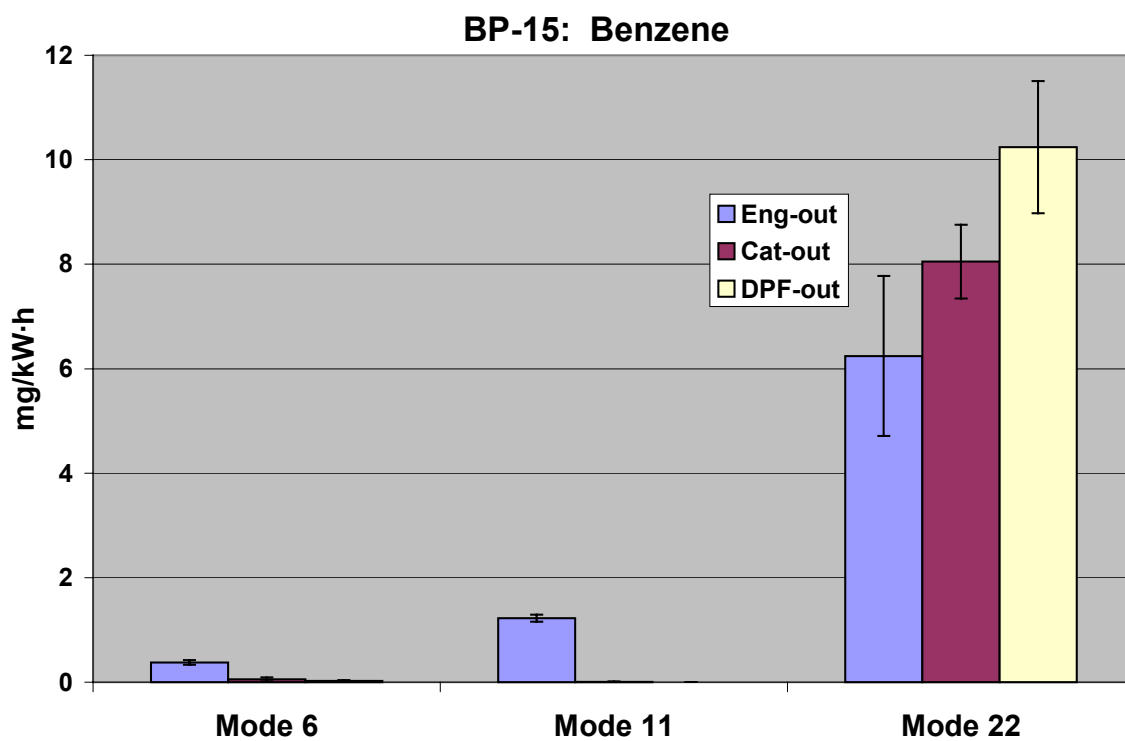


Figure E-14. Benzene Emissions with BP-15 Fuel

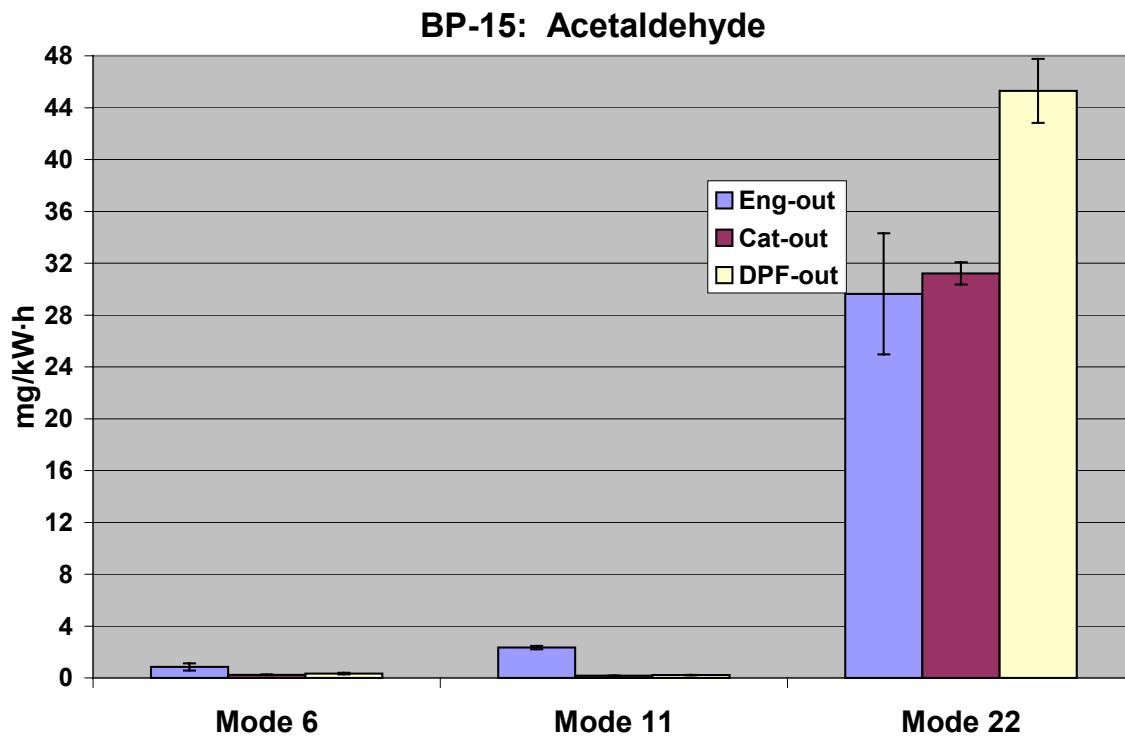


Figure E-15. Acetaldehyde Emissions with BP-15 Fuel

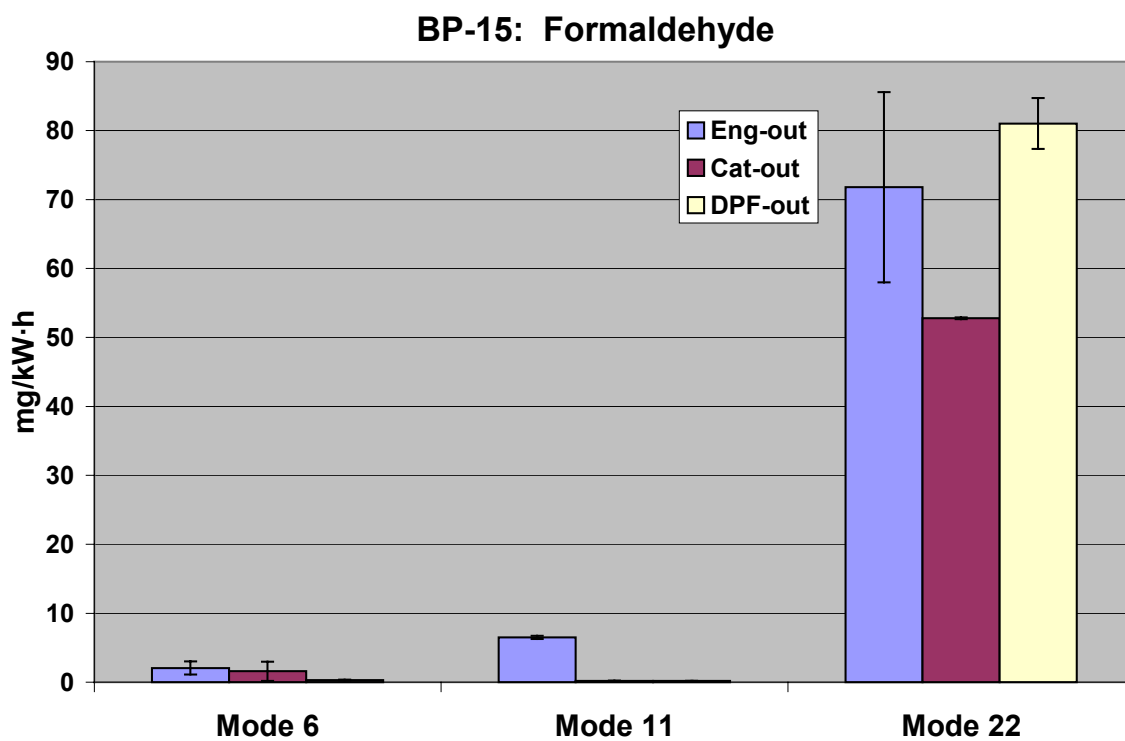


Figure E-16. Formaldehyde Emissions with BP-15 Fuel



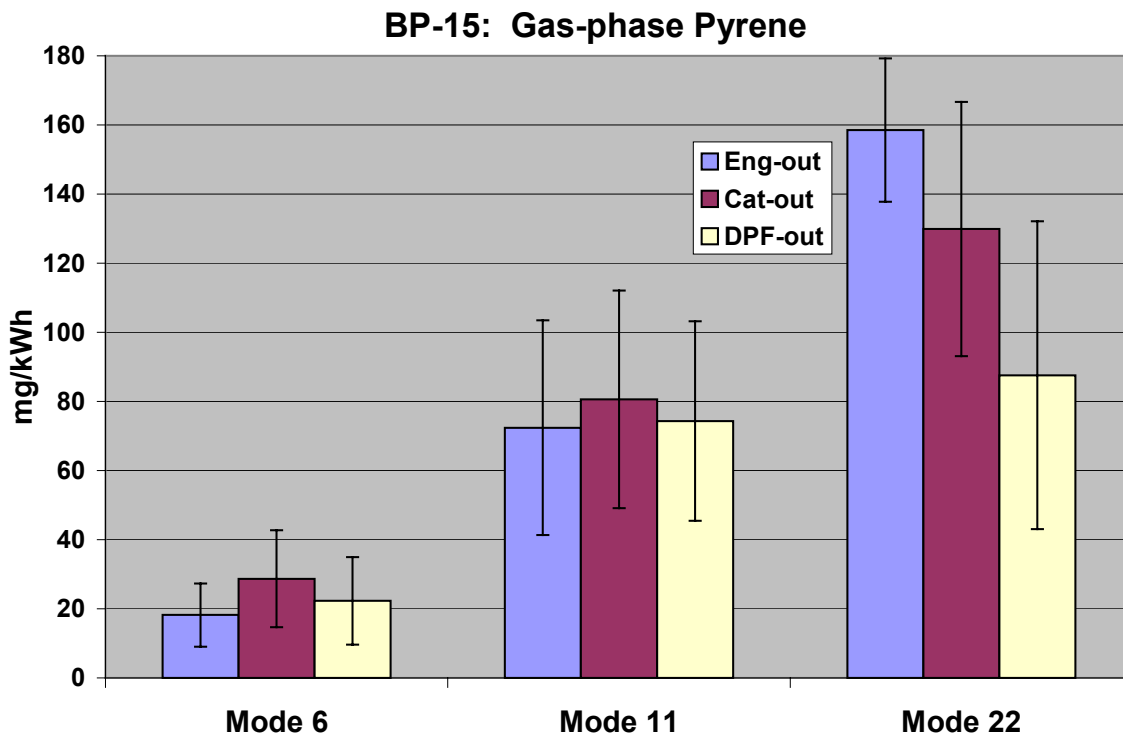


Figure E-17. Gas-Phase Pyrene Emissions with BP-15 Fuel

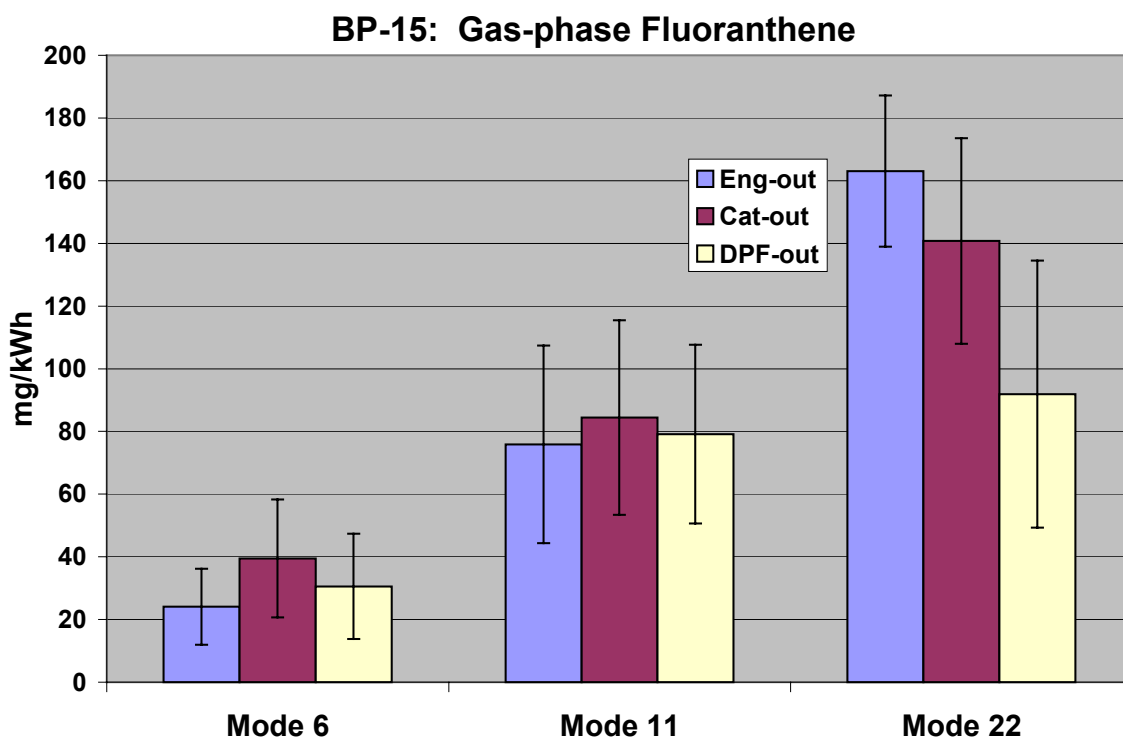


Figure E-18. Gas-Phase Fluoranthene Emissions with BP-15 Fuel

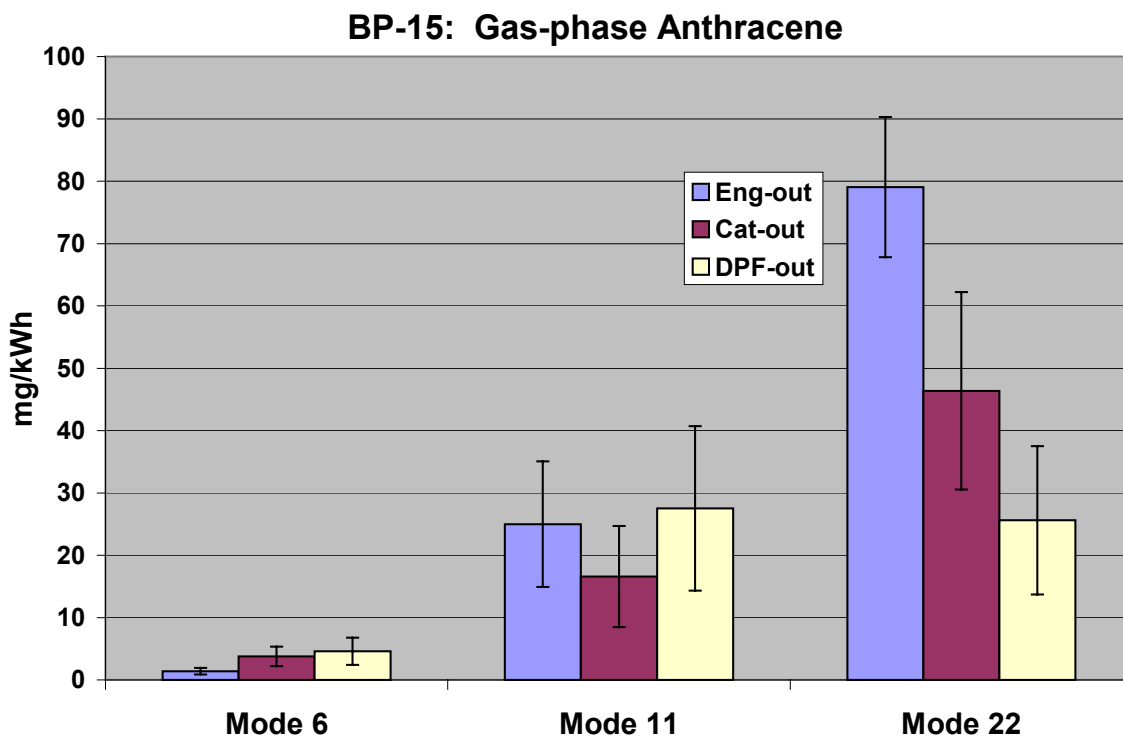


Figure E-19. Gas-Phase Anthracene Emissions with BP-15 Fuel

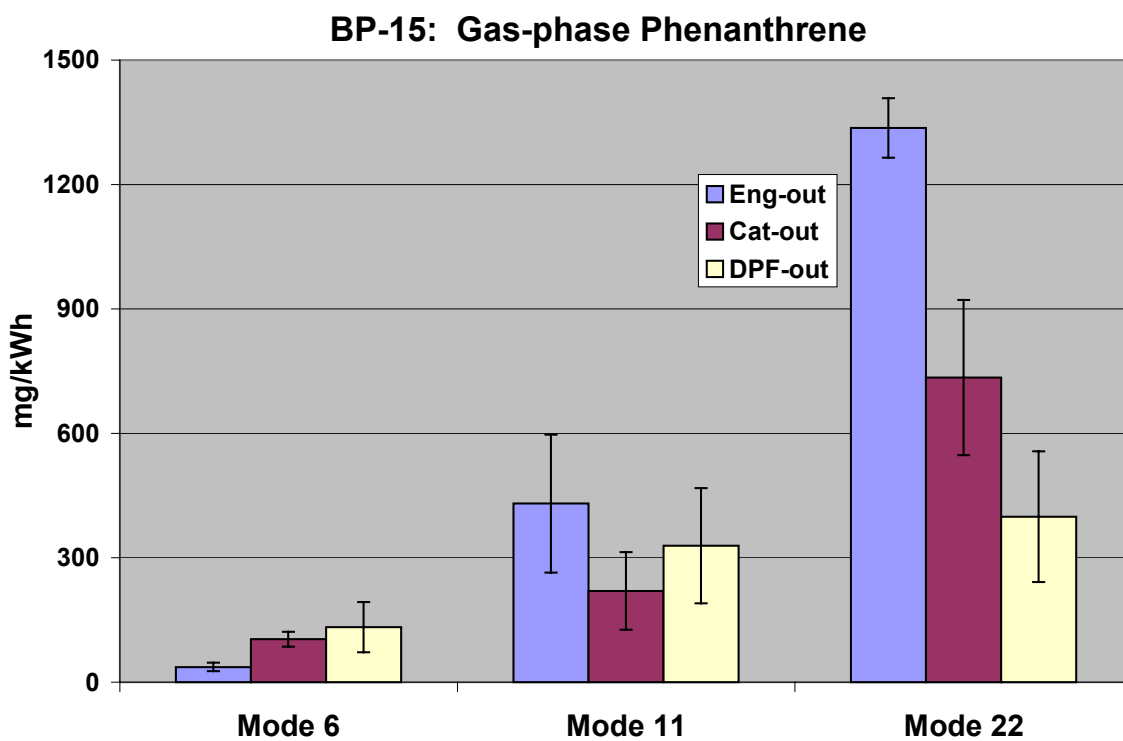


Figure E-20. Gas-Phase Phenanthrene Emissions with BP-15 Fuel

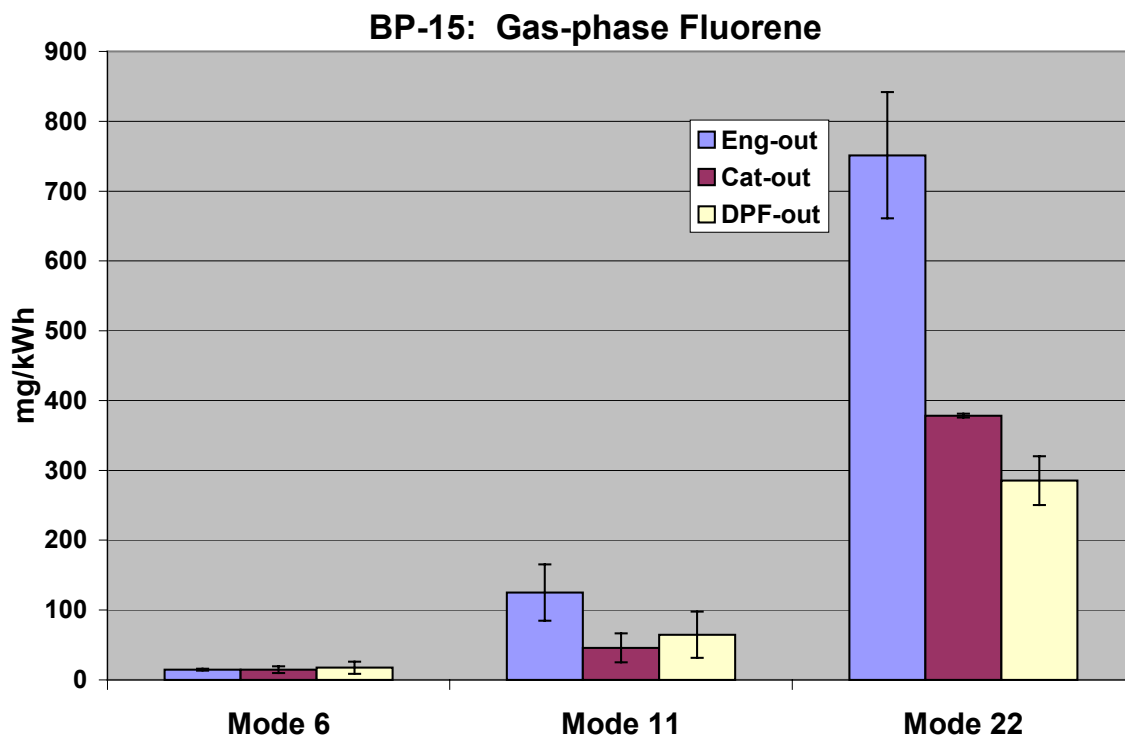


Figure E-21. Gas-Phase Fluorene Emissions with BP-15 Fuel

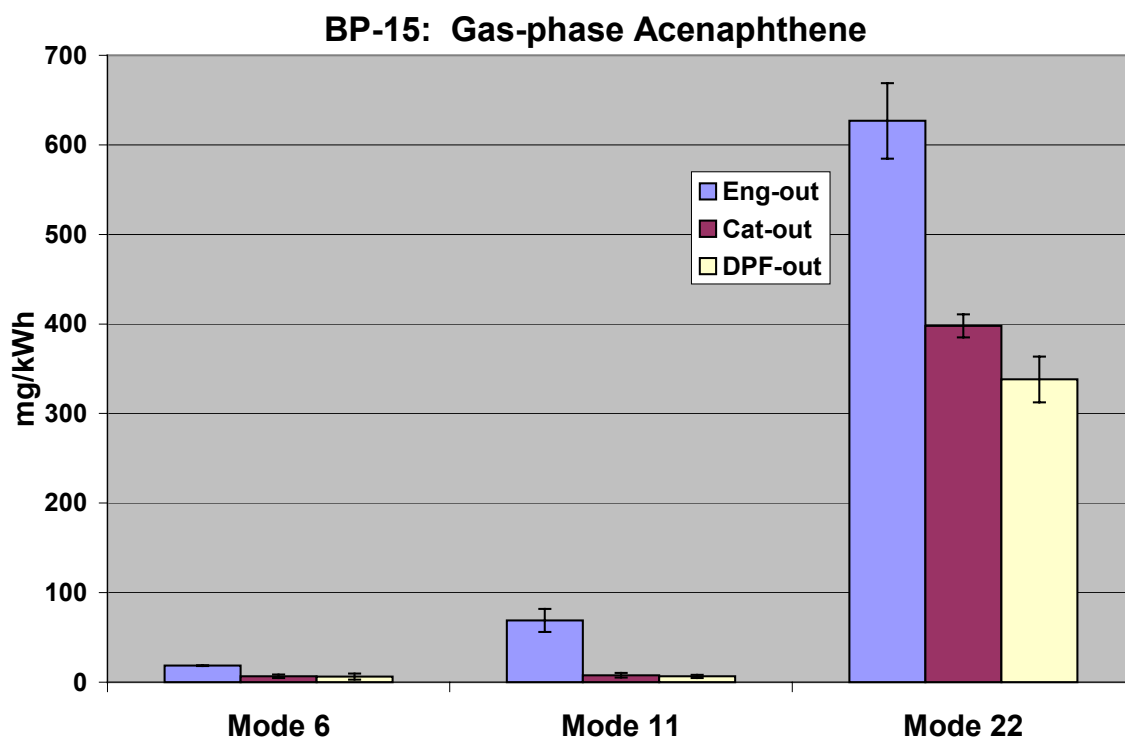


Figure E-22. Gas-Phase Acenaphthene Emissions with BP-15 Fuel

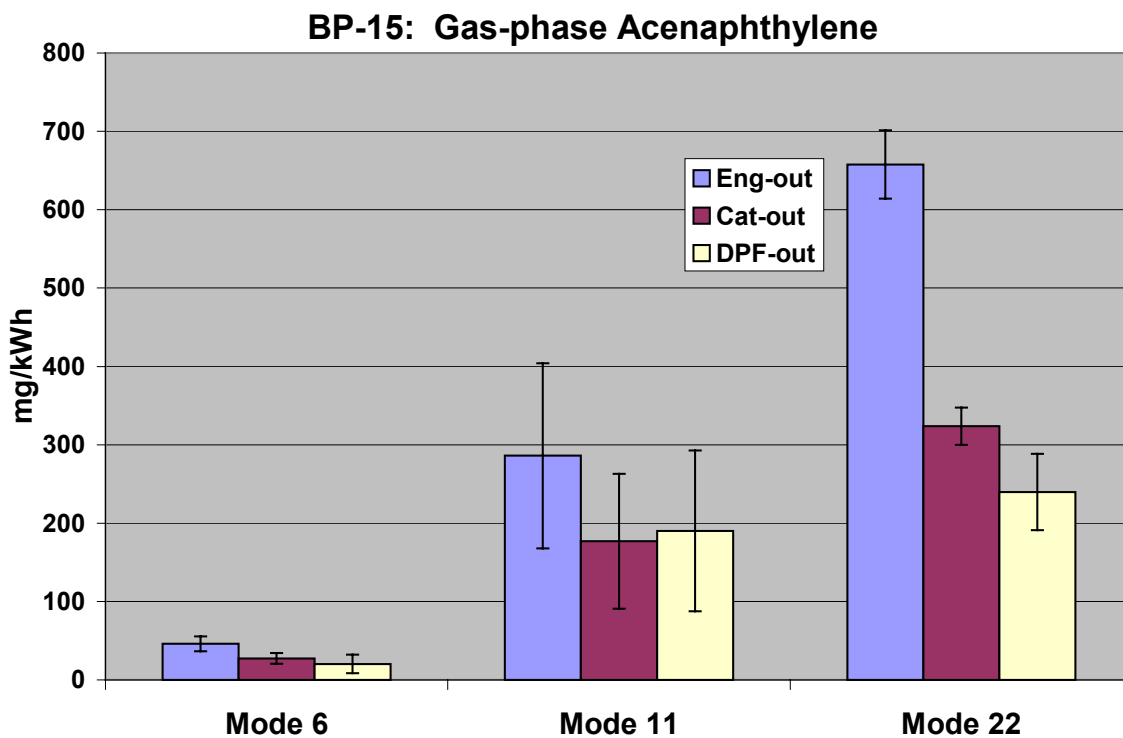


Figure E-23. Gas-Phase Acenaphthylene Emissions with BP-15 Fuel

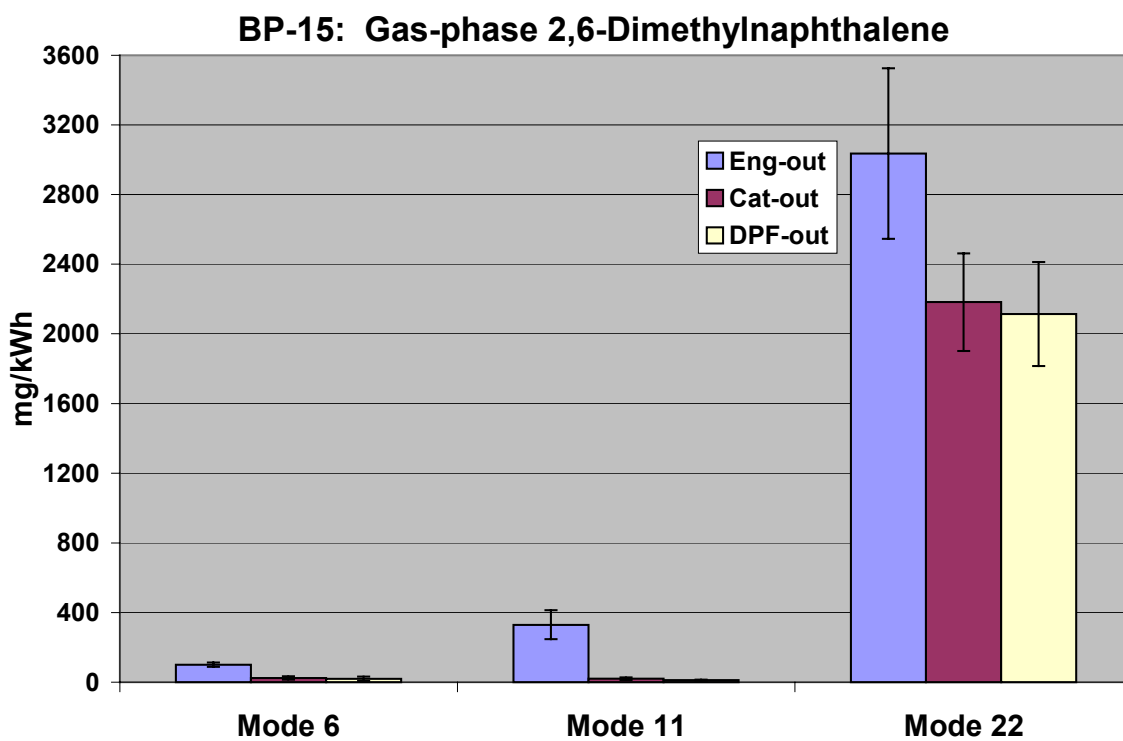


Figure E-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions with BP-15 Fuel

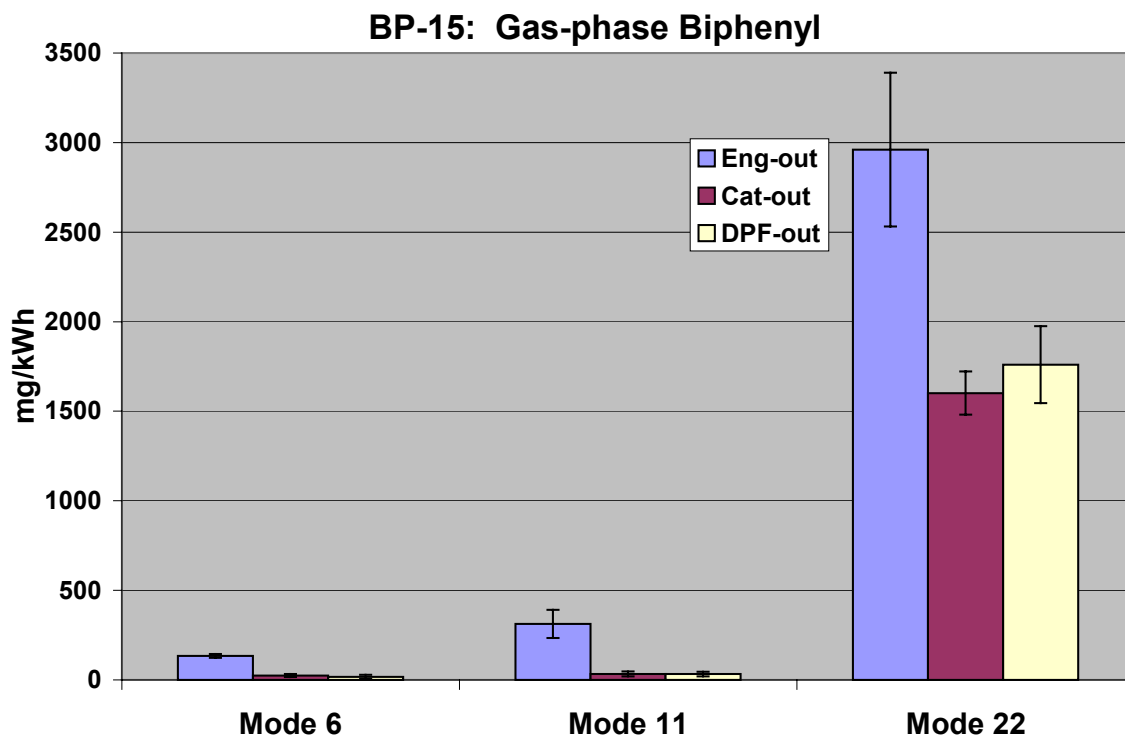


Figure E-25. Gas-Phase Biphenyl Emissions with BP-15 Fuel

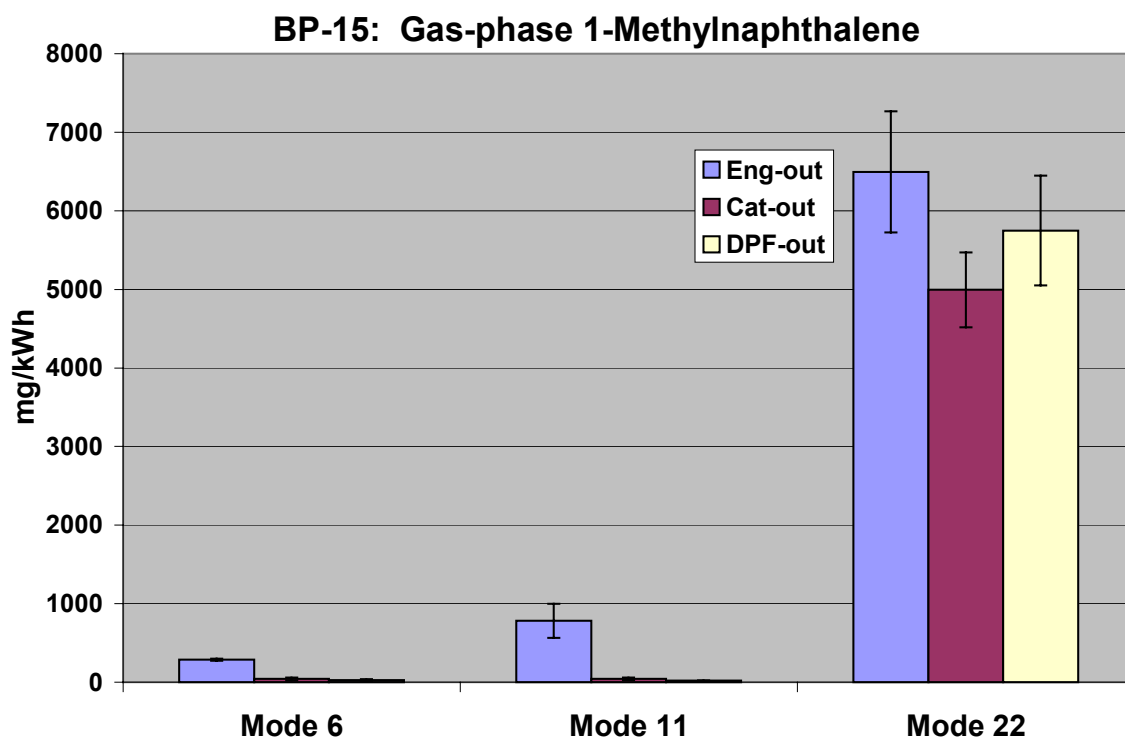


Figure E-26. Gas-Phase 1-Methylnaphthalene Emissions with BP-15 Fuel

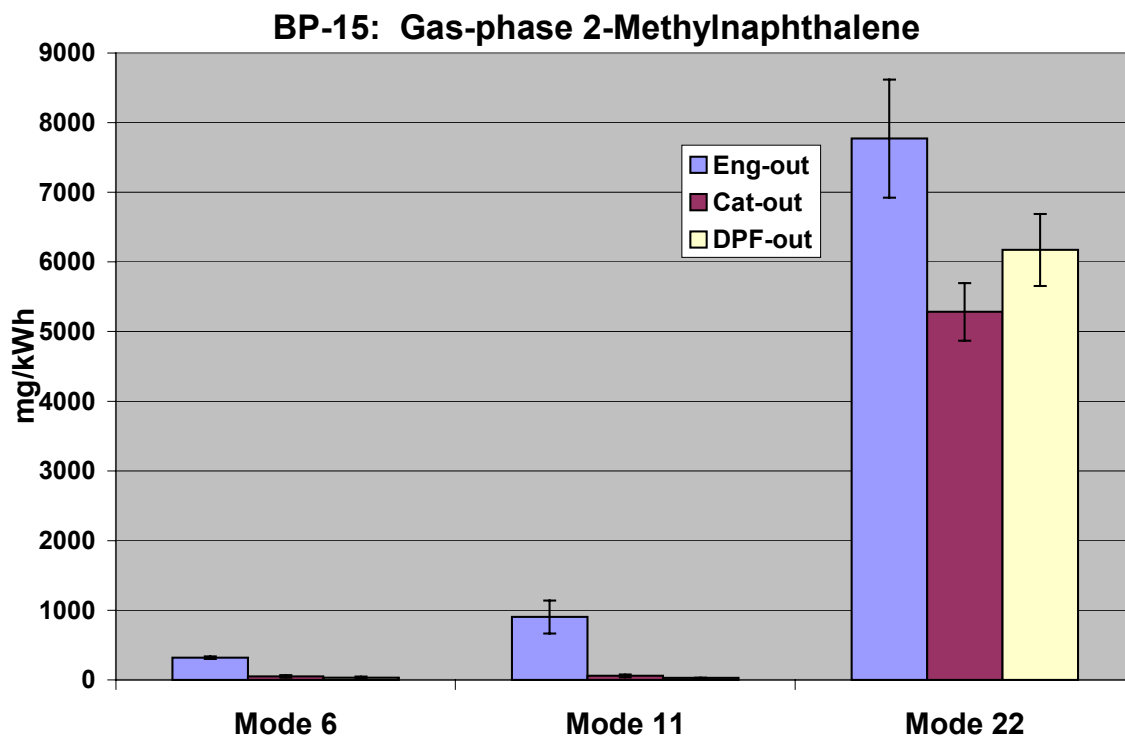


Figure E-27. Gas-Phase 2-Methylnaphthalene Emissions with BP-15 Fuel

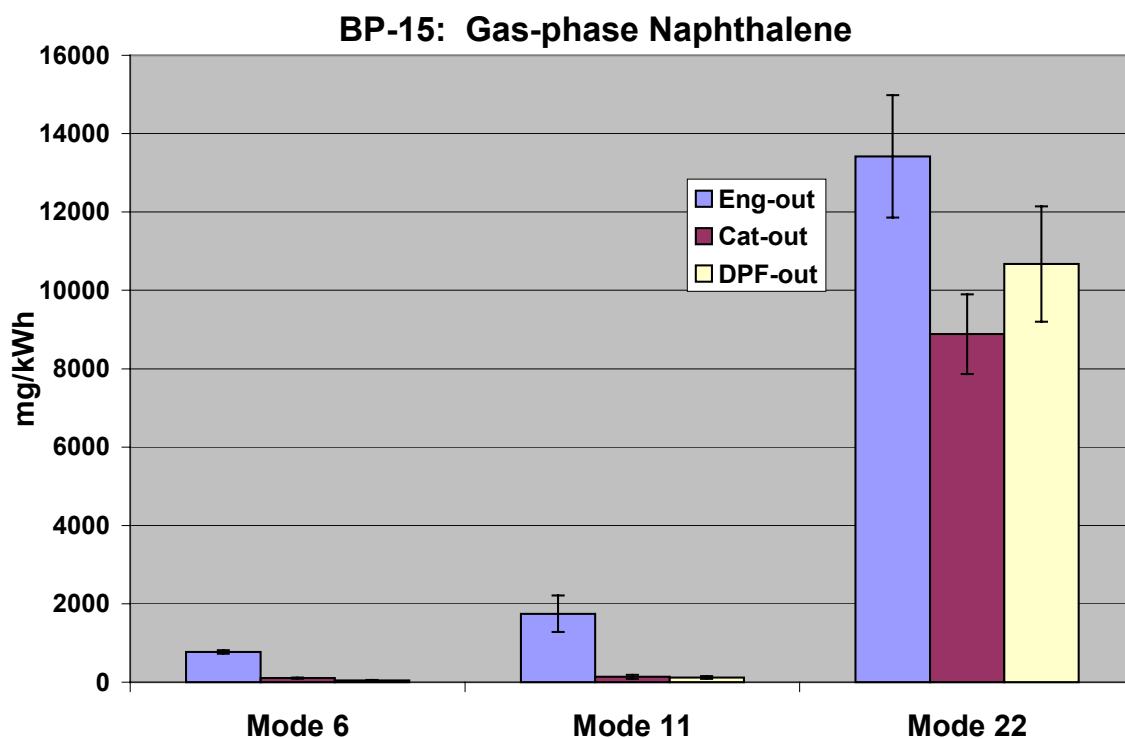


Figure E-28. Gas-Phase Naphthalene Emissions with BP-15 Fuel

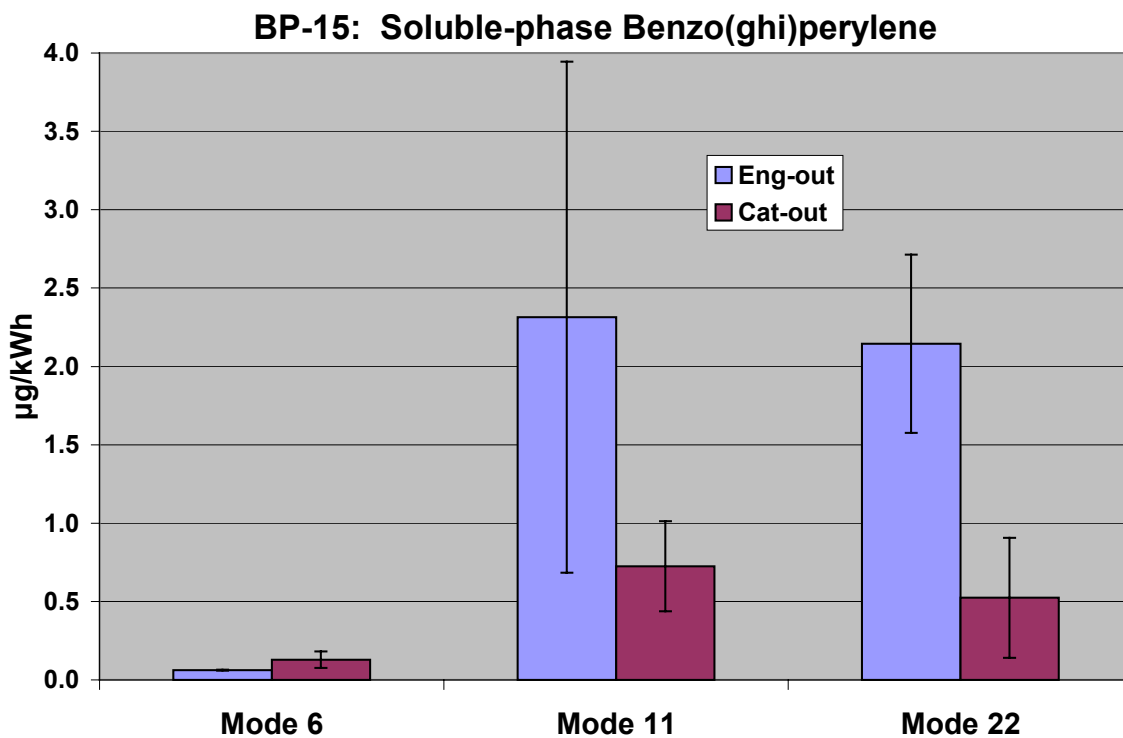


Figure E-29. Soluble-Phase Benzo(ghi)perylene Emissions with BP-15 Fuel

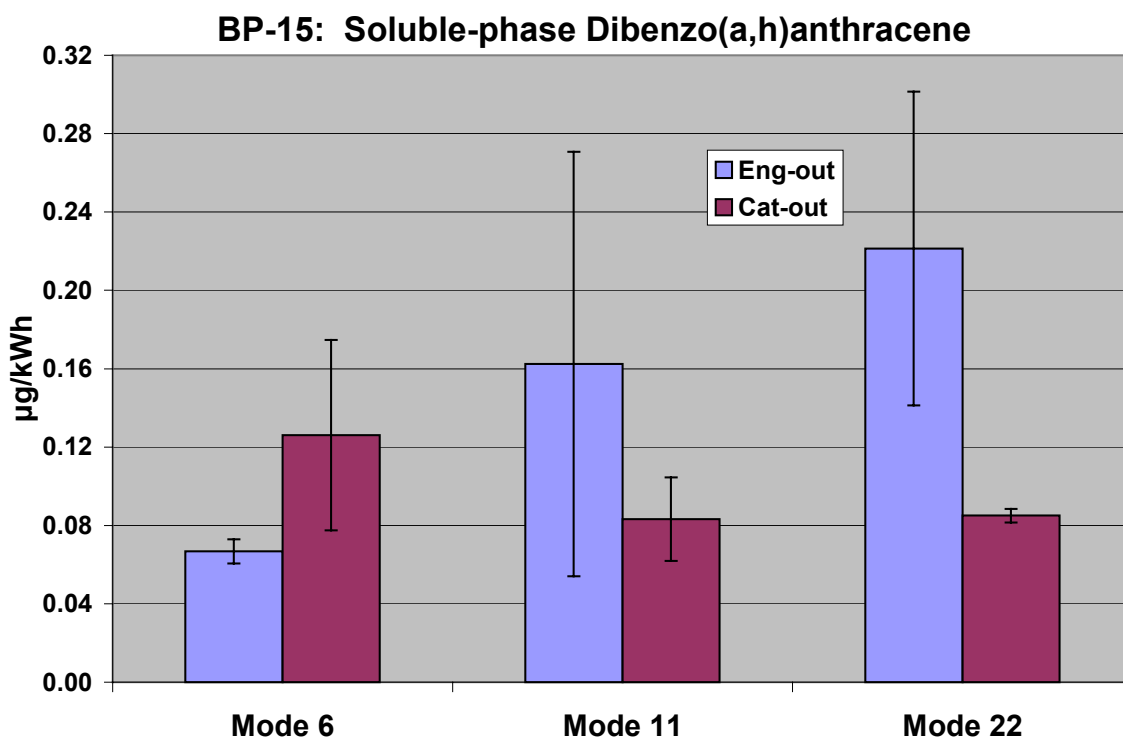


Figure E-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions with BP-15 Fuel

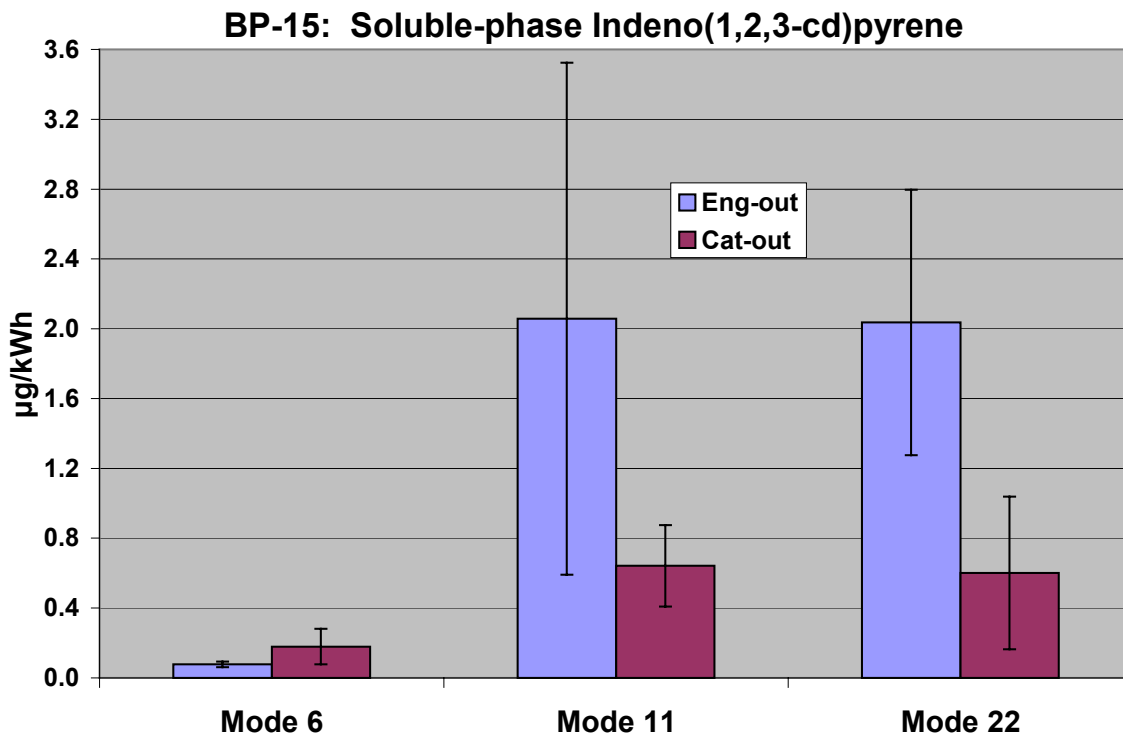


Figure E-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions with BP-15 Fuel

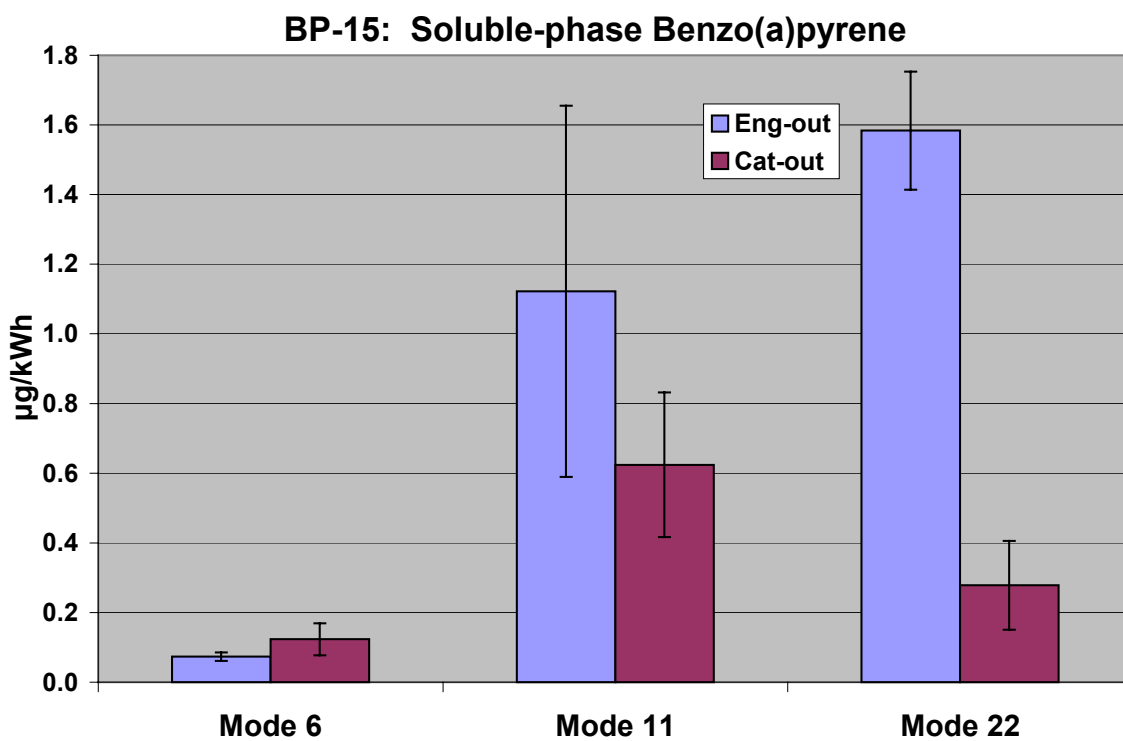


Figure E-32. Soluble-Phase Benzo(a)pyrene Emissions with BP-15 Fuel



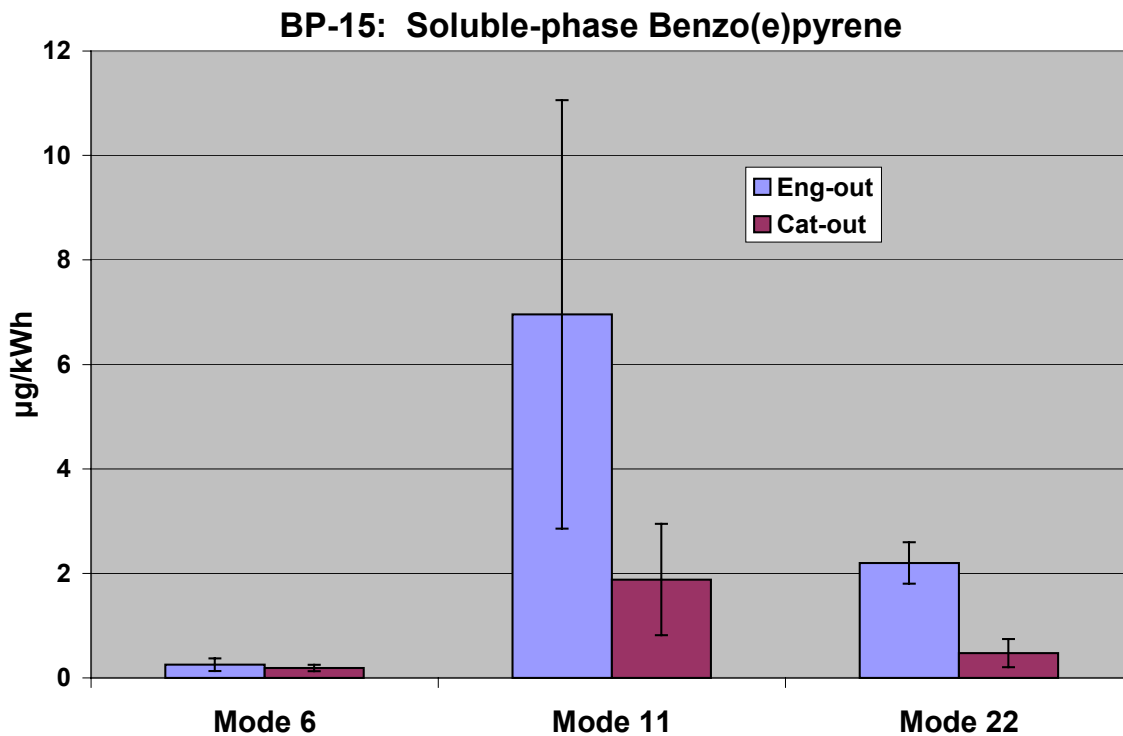


Figure E-33. Soluble-Phase Benzo(e)pyrene Emissions with BP-15 Fuel

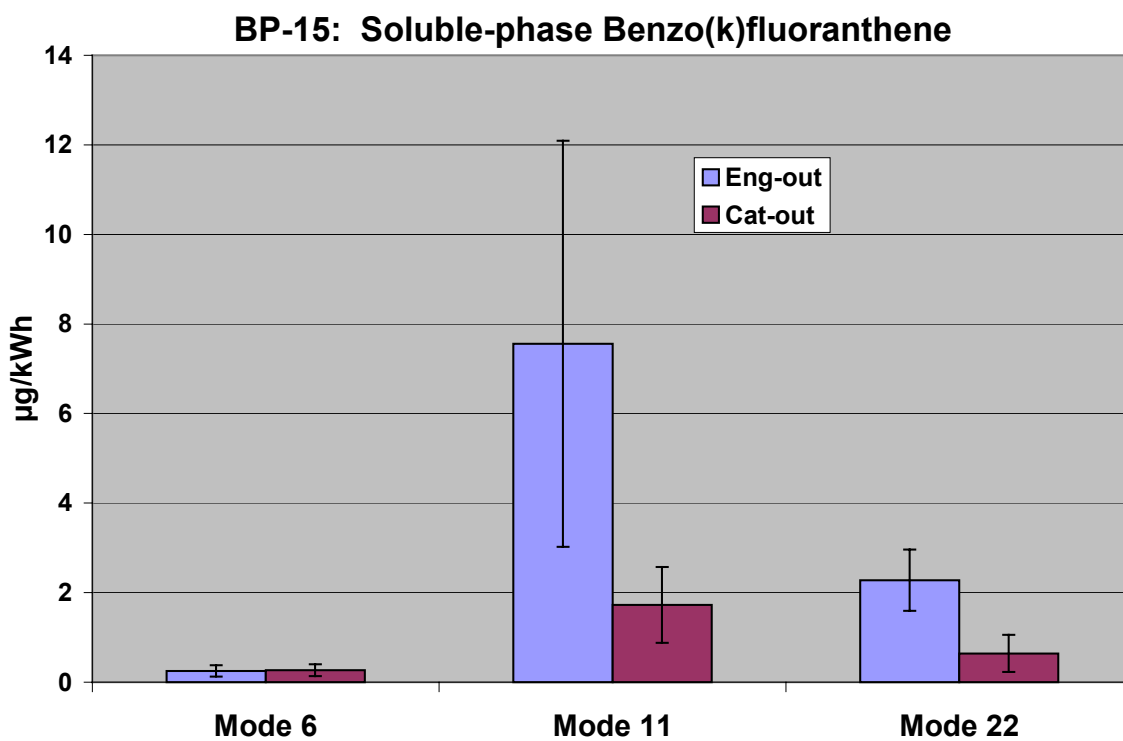


Figure E-34. Soluble-Phase Benzo(k)fluoranthene Emissions with BP-15 Fuel

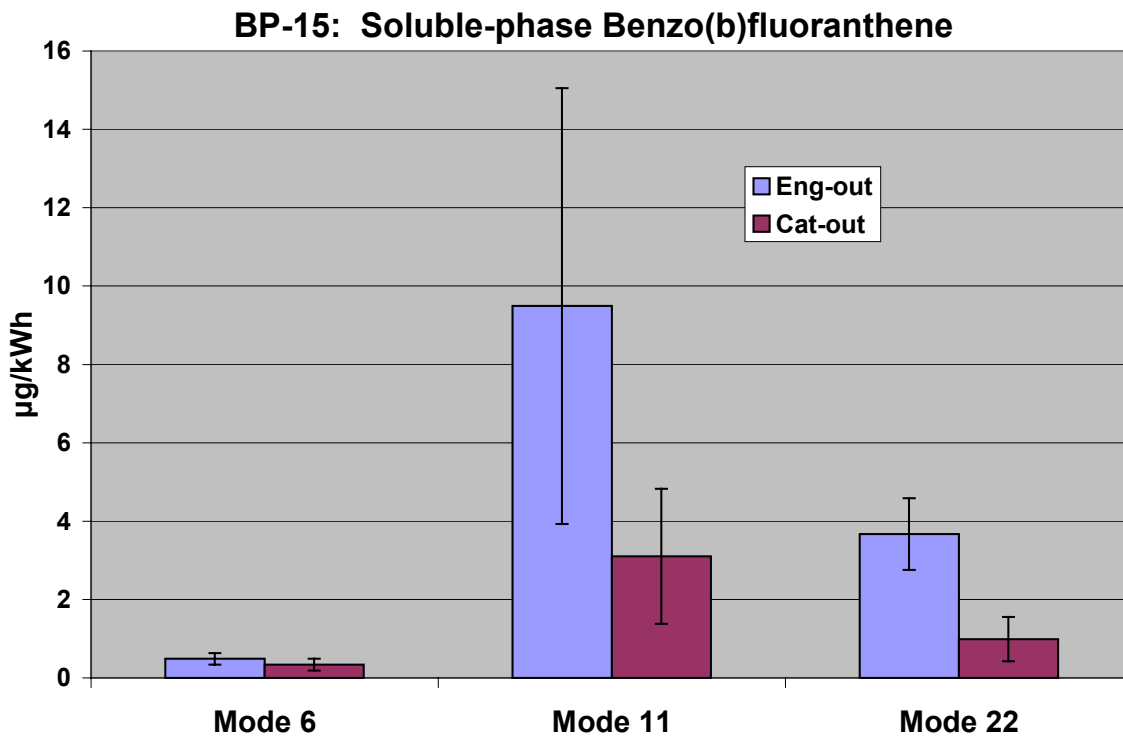


Figure E-35. Soluble-Phase Benzo(b)fluoranthene Emissions with BP-15 Fuel

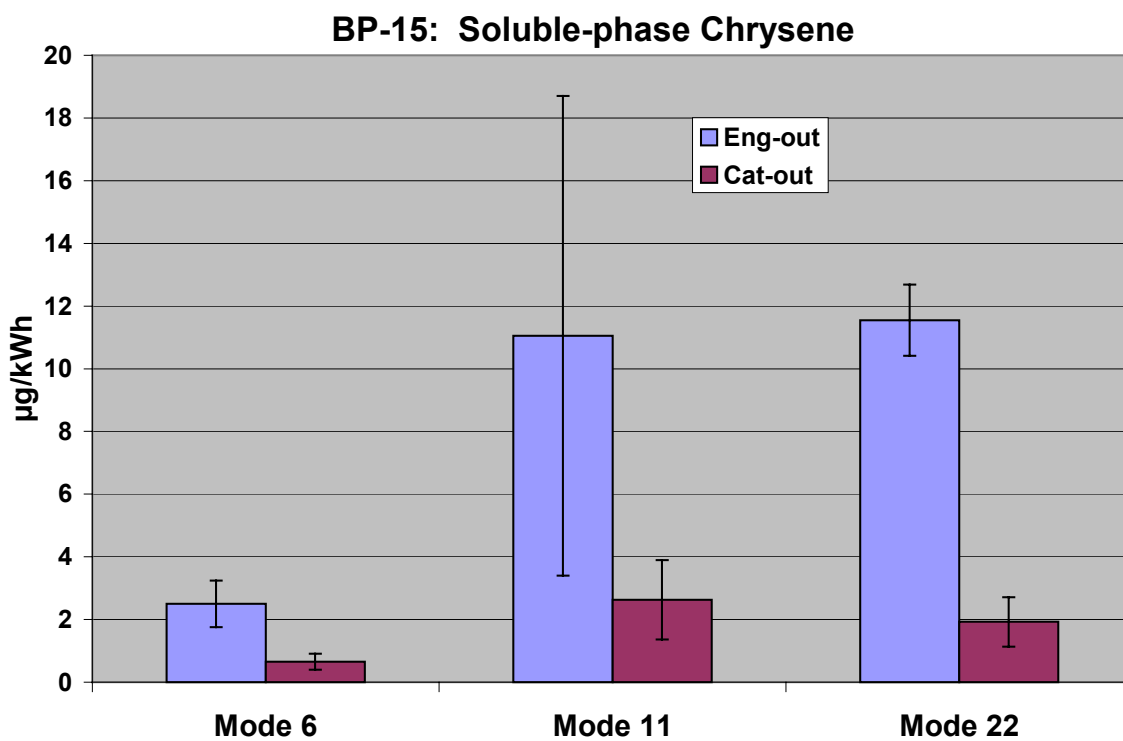


Figure E-36. Soluble-Phase Chrysene Emissions with BP-15 Fuel

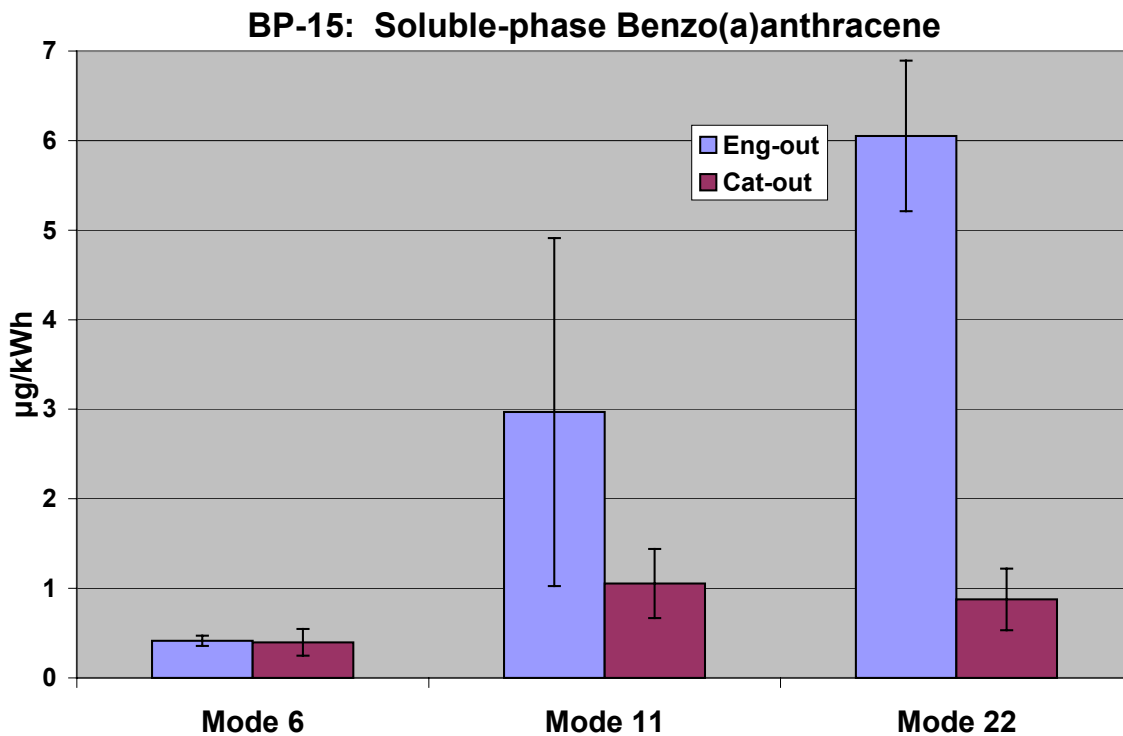


Figure E-37. Soluble-Phase Benzo(a)anthracene Emissions with BP-15 Fuel

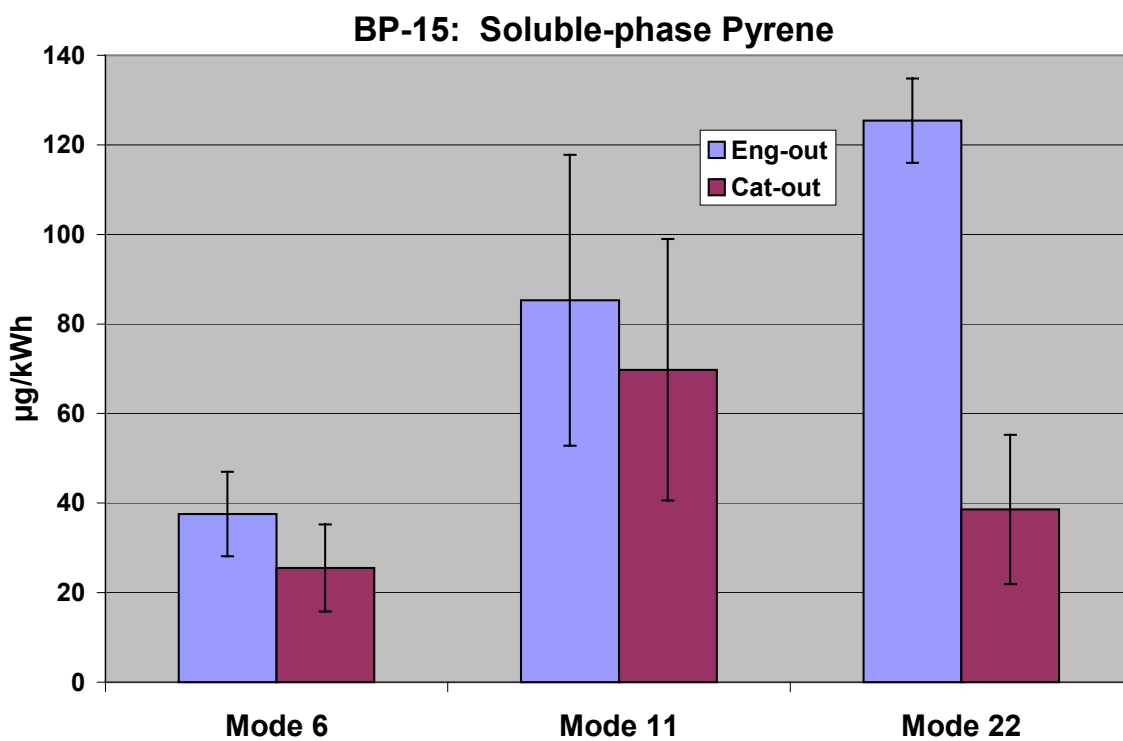


Figure E-38. Soluble-Phase Pyrene Emissions with BP-15 Fuel

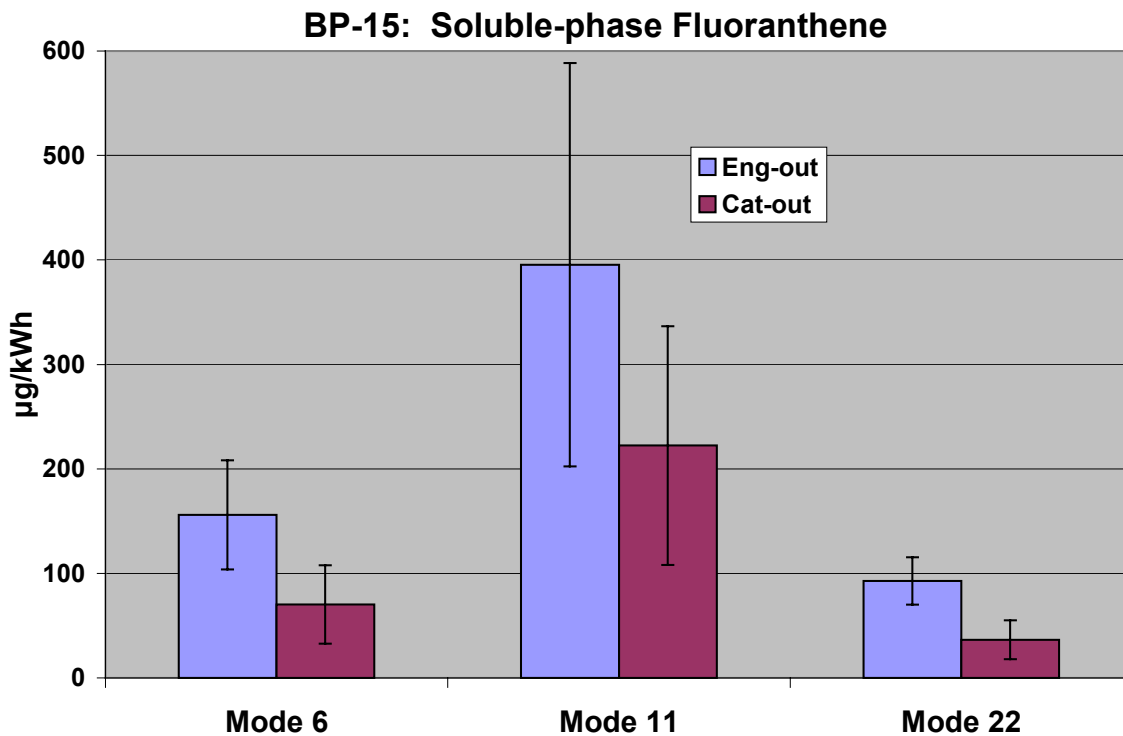


Figure E-39. Soluble-Phase Fluoranthene Emissions with BP-15 Fuel

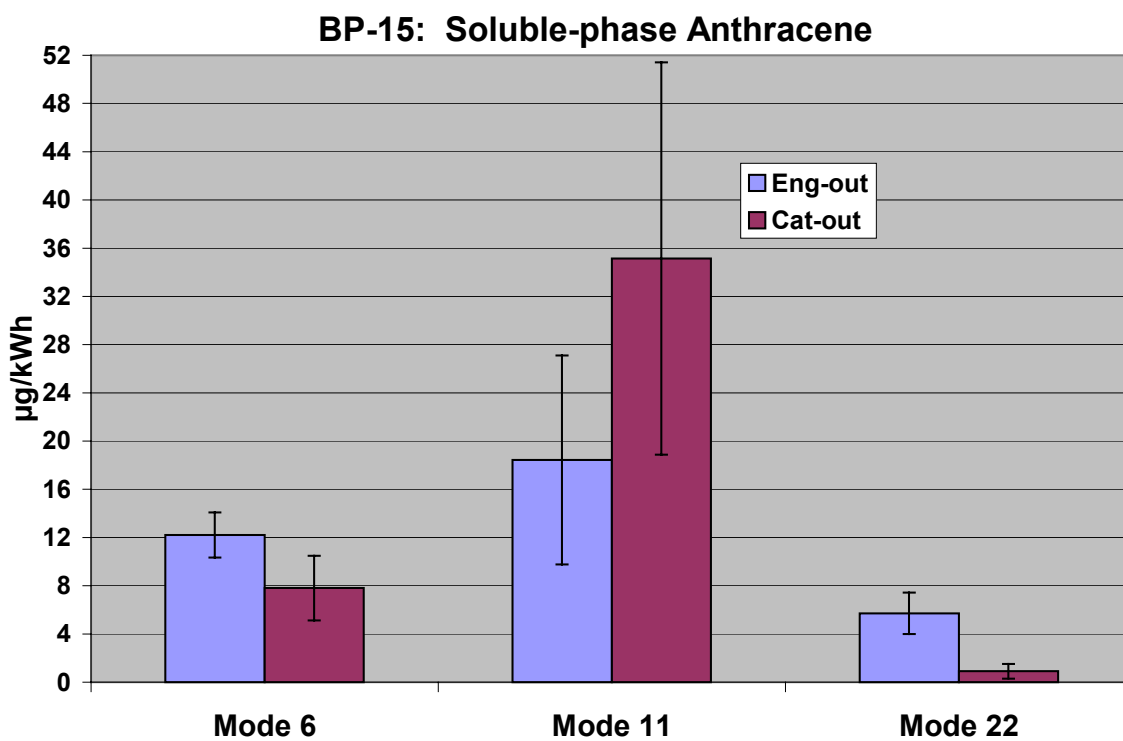


Figure E-40. Soluble-Phase Anthracene Emissions with BP-15 Fuel

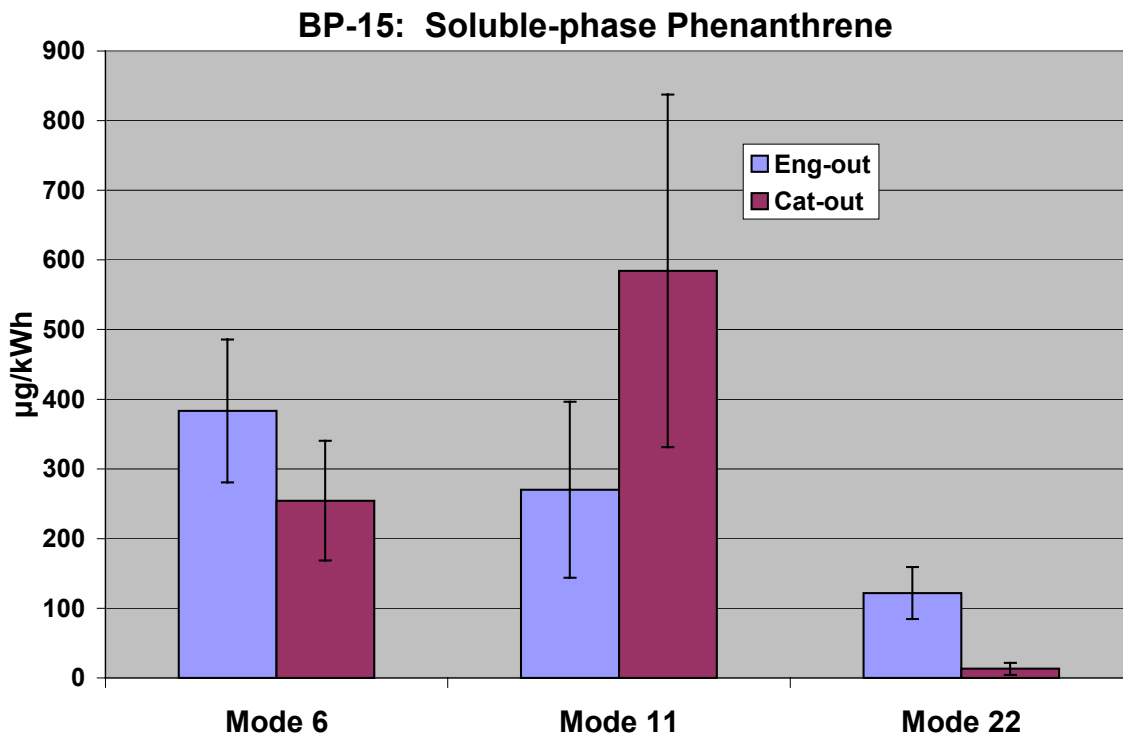


Figure E-41. Soluble-Phase Phenanthrene Emissions with BP-15 Fuel

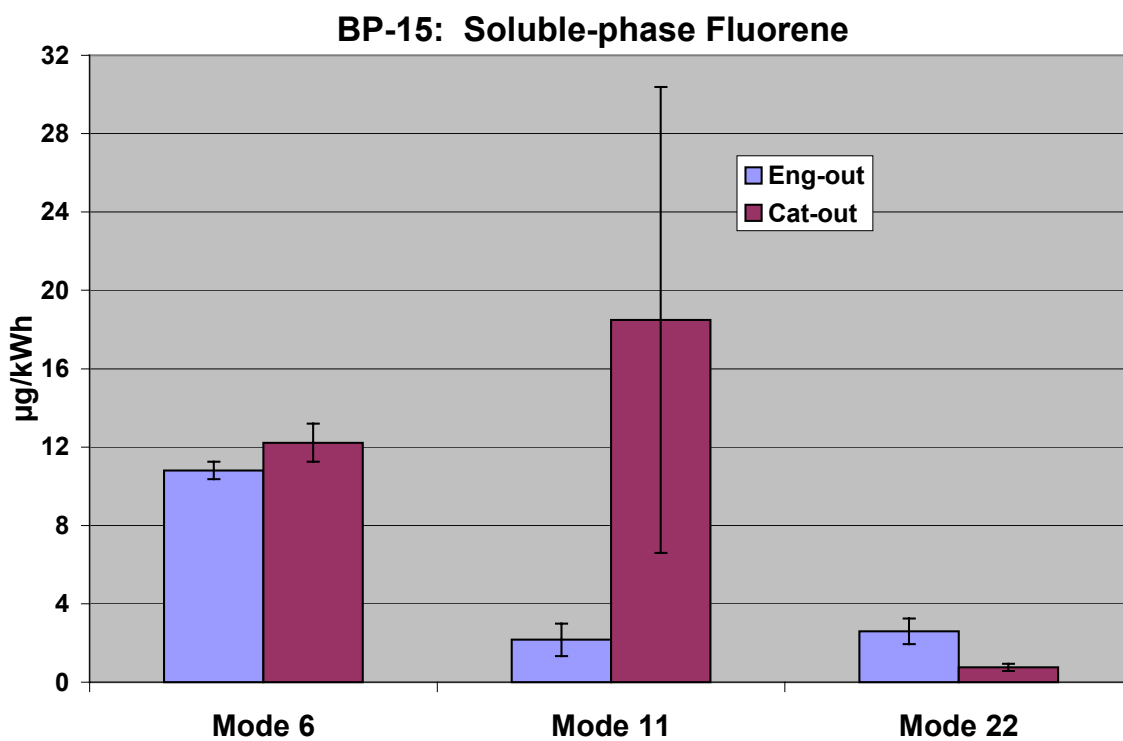


Figure E-42. Soluble-Phase Fluorene Emissions with BP-15 Fuel

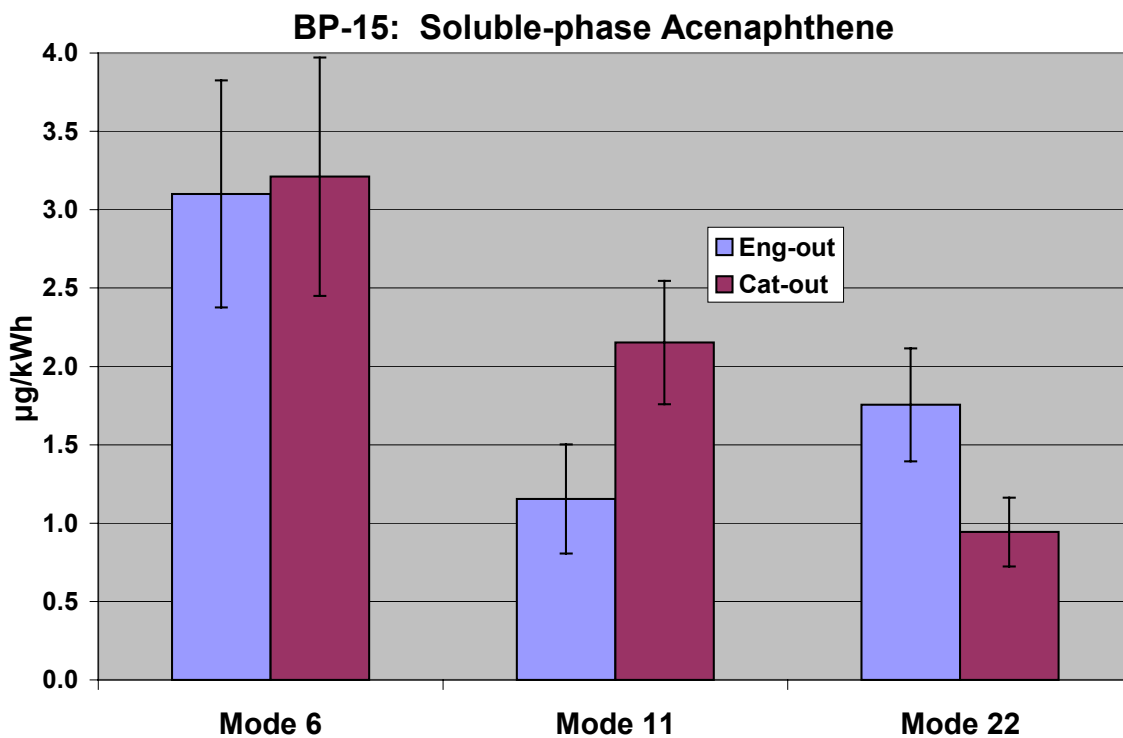


Figure E-43. Soluble-Phase Acenaphthene Emissions with BP-15 Fuel

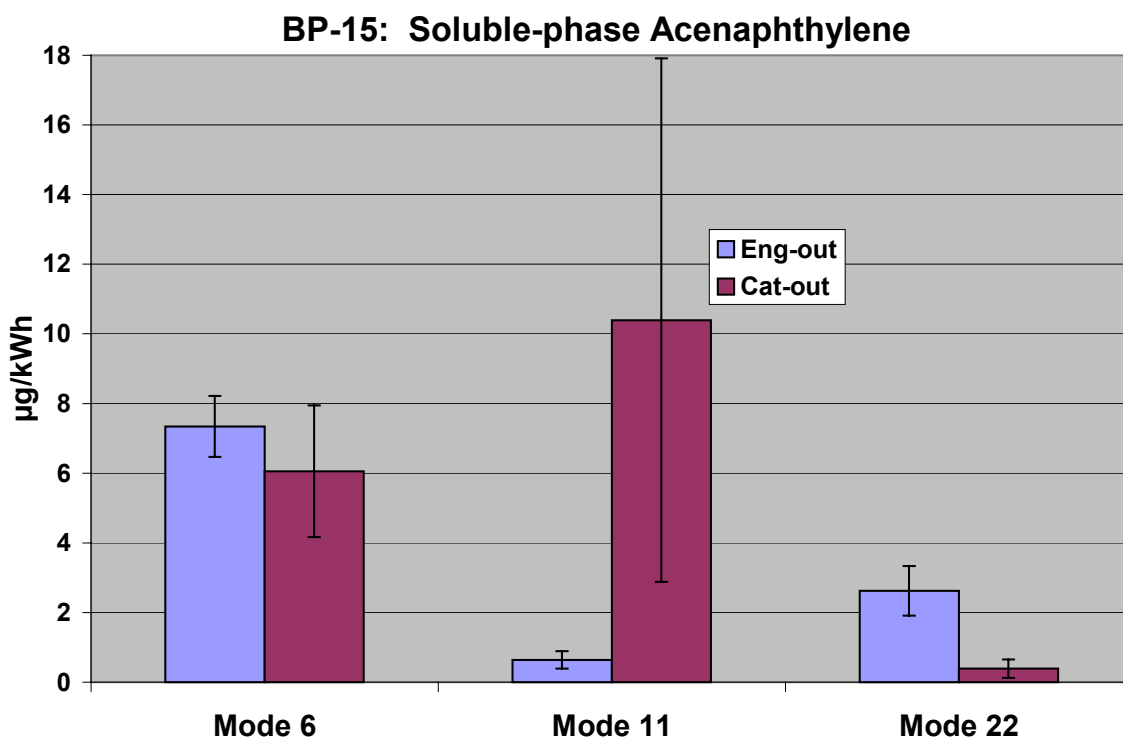


Figure E-44. Soluble-Phase Acenaphthylene Emissions with BP-15 Fuel

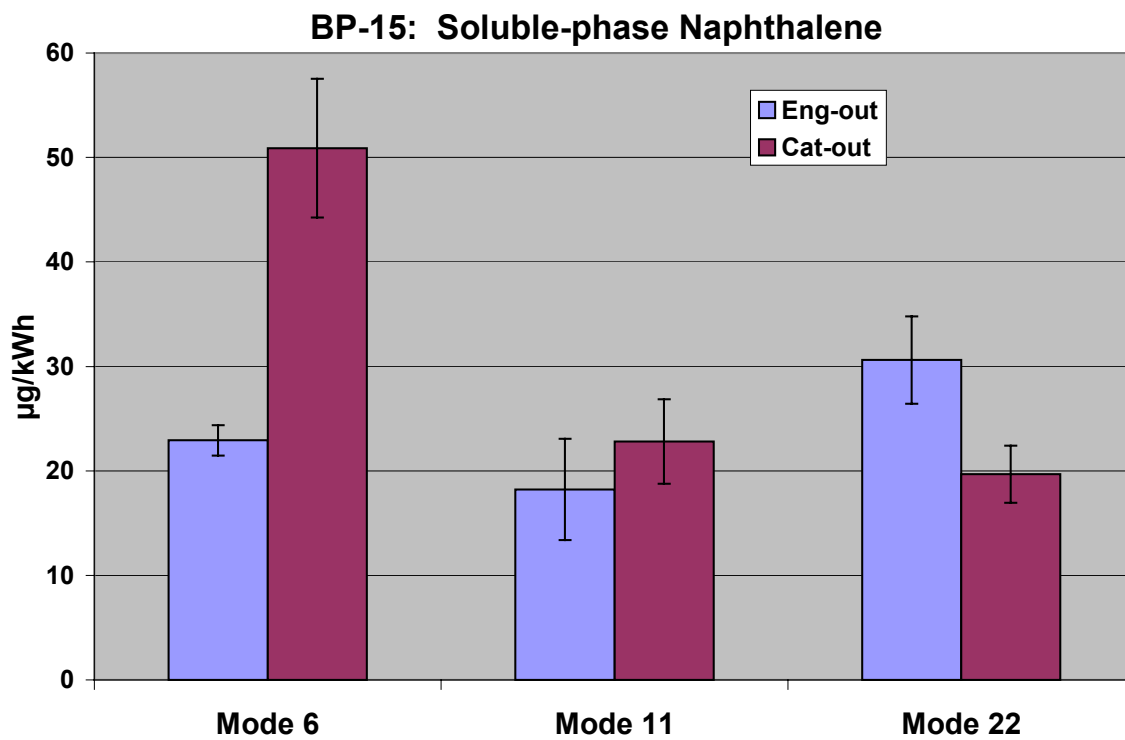


Figure E-45. Soluble-Phase Naphthalene Emissions with BP-15 Fuel

## **APPENDIX F**

### **BP15+DBM Fuel Operation Test Results**



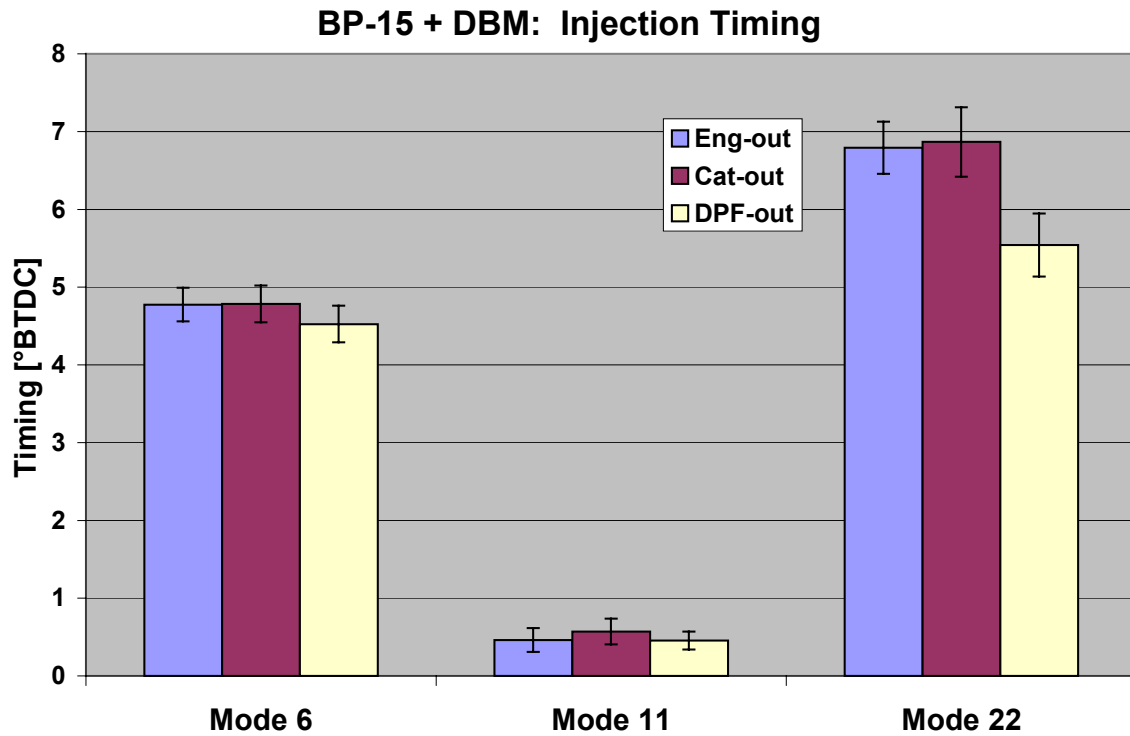


Figure F-1. Injection Timing with DBM Fuel Additive

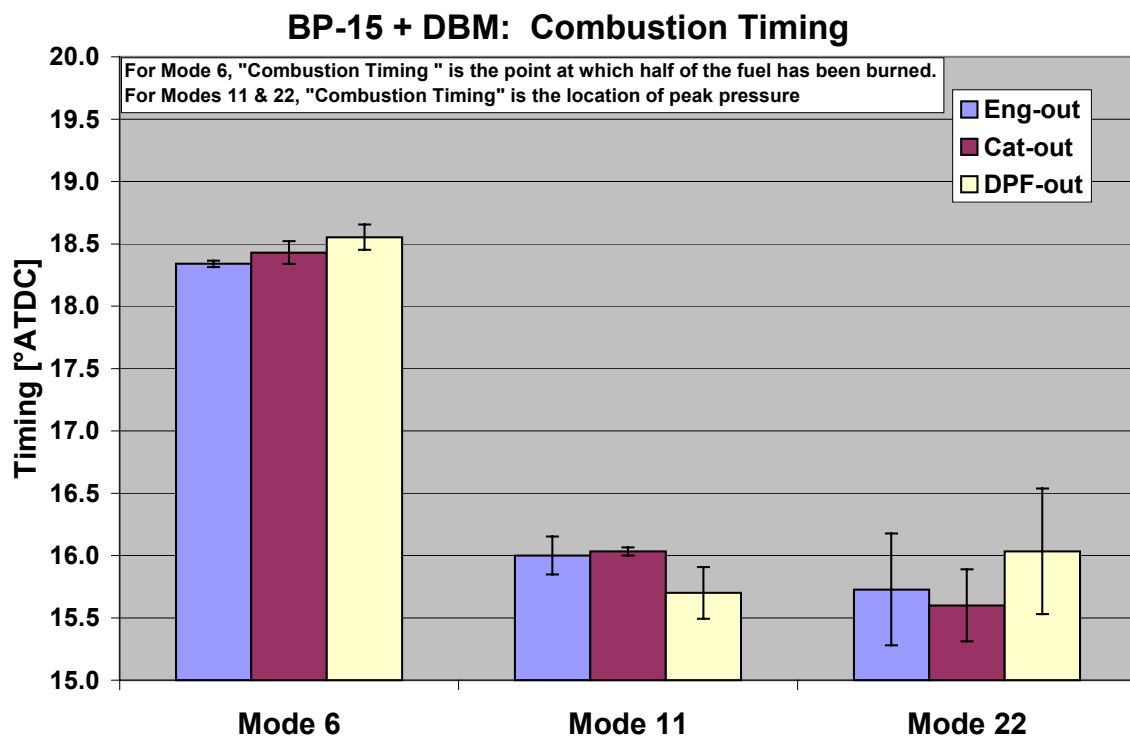


Figure F-2. Combustion Timing with DBM Fuel Additive

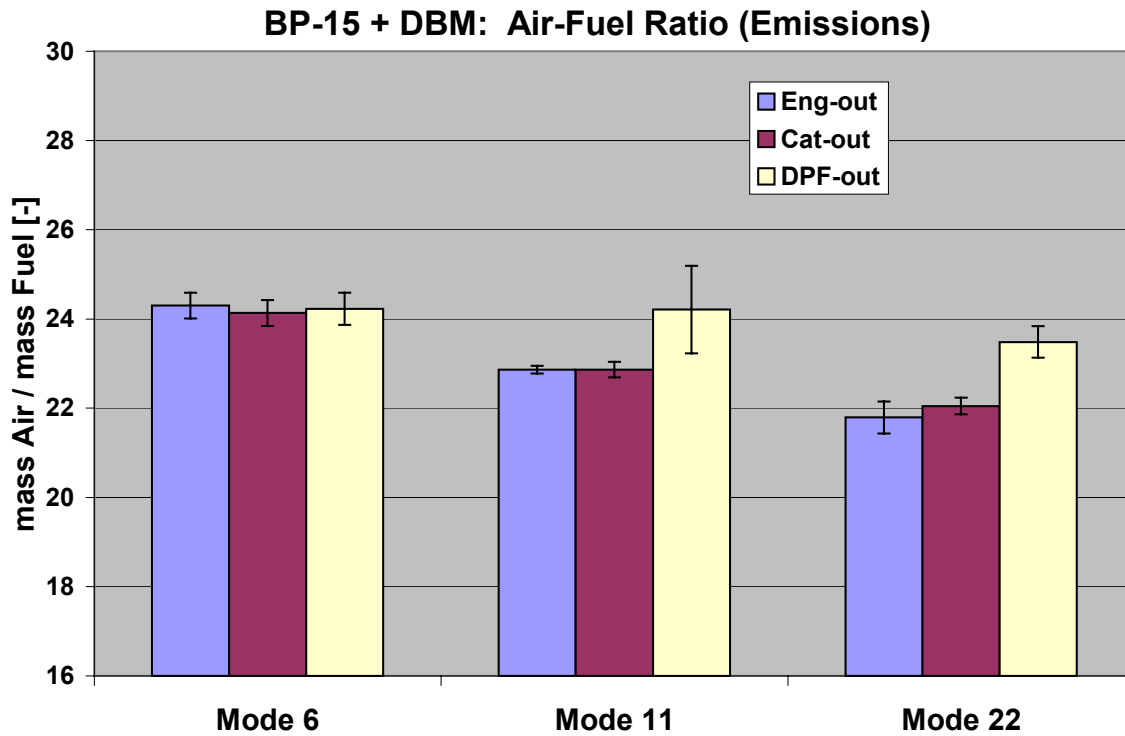


Figure F-3. Emissions Air-Fuel Ratio with DBM Fuel Additive

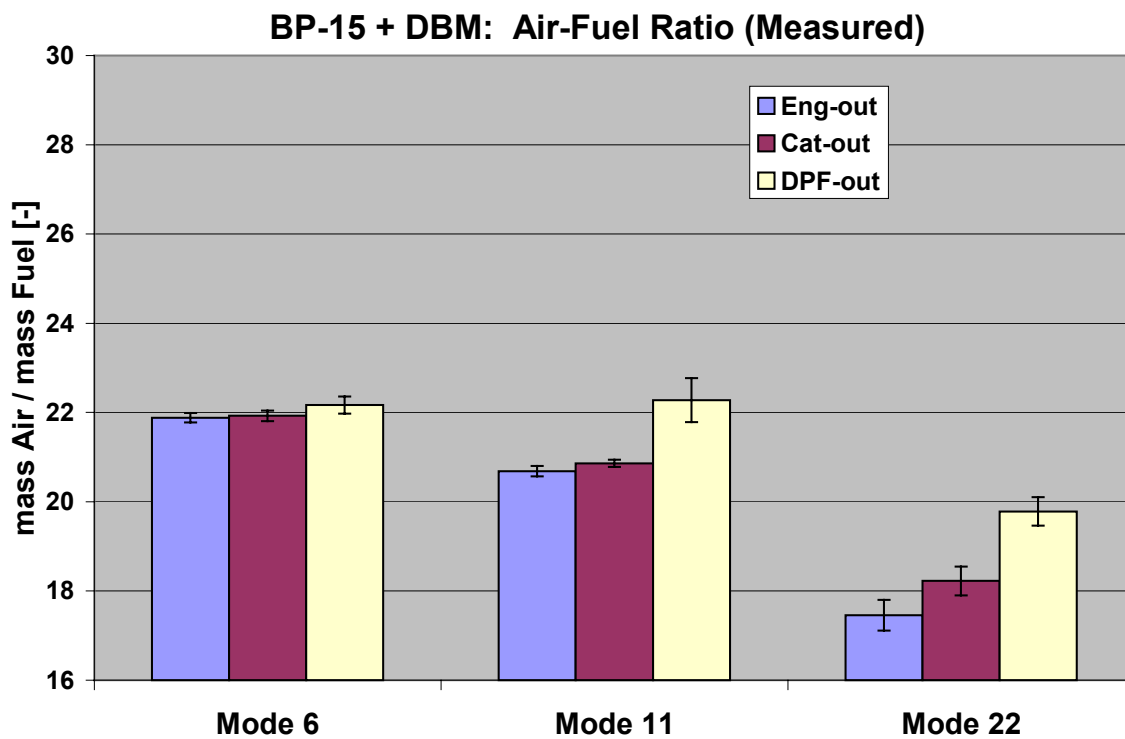


Figure F-4. Measured Air-Fuel Ratio with DBM Fuel Additive

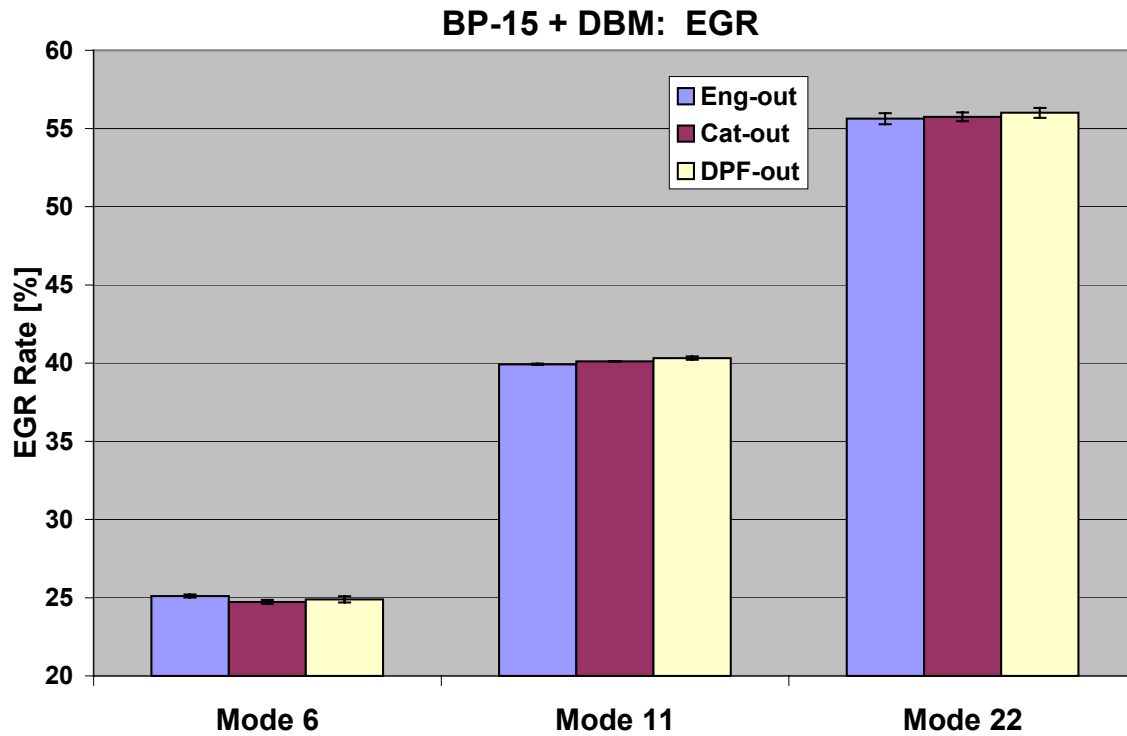


Figure F-5. EGR Rate with DBM Fuel Additive

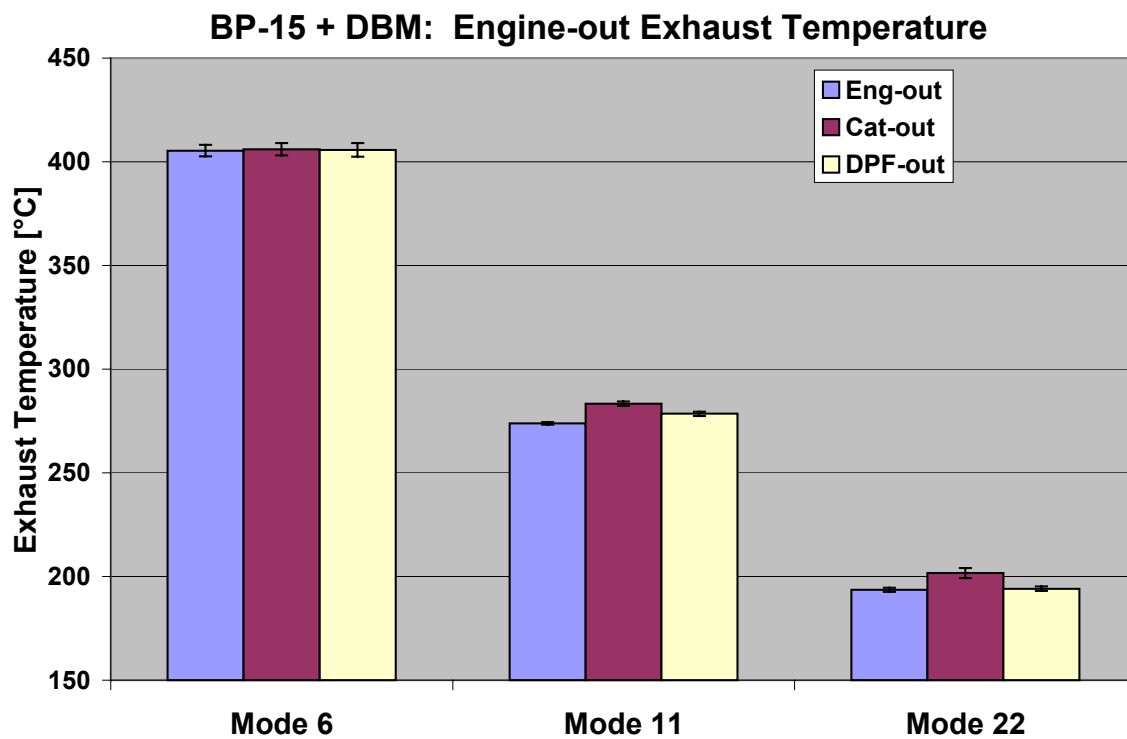


Figure F-6. Engine-Out Exhaust Temperature with DBM Fuel Additive

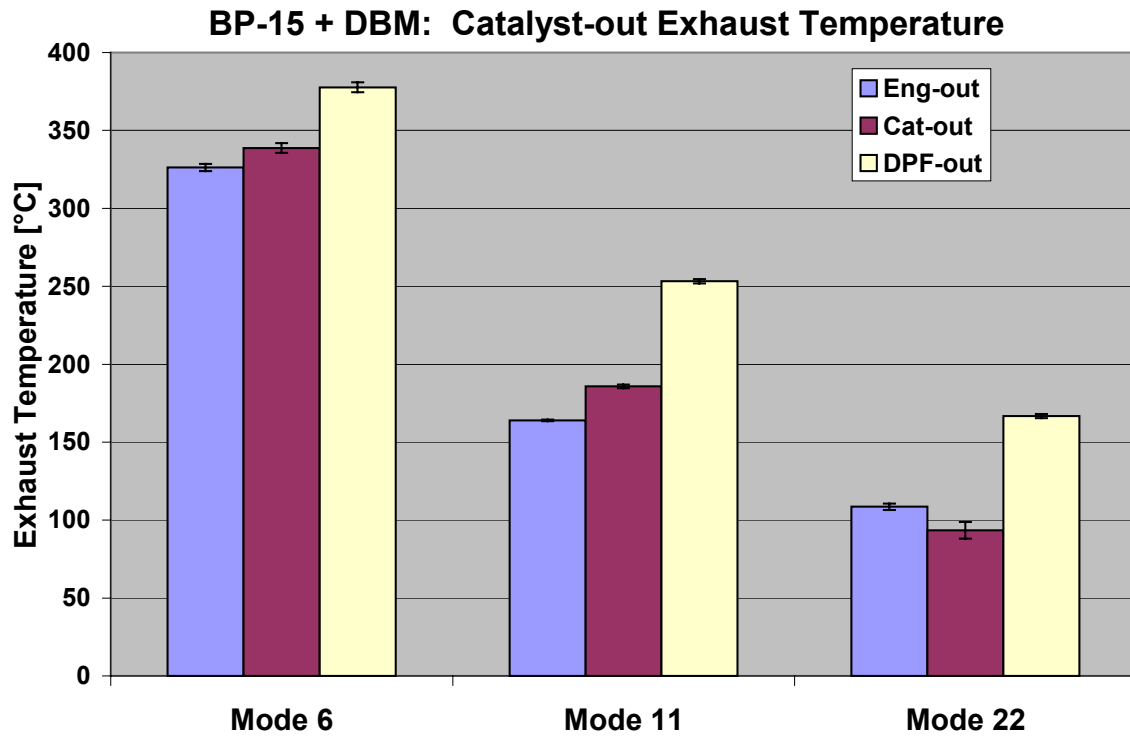


Figure F-7. Catalyst-Out Exhaust Temperature with DBM Fuel Additive

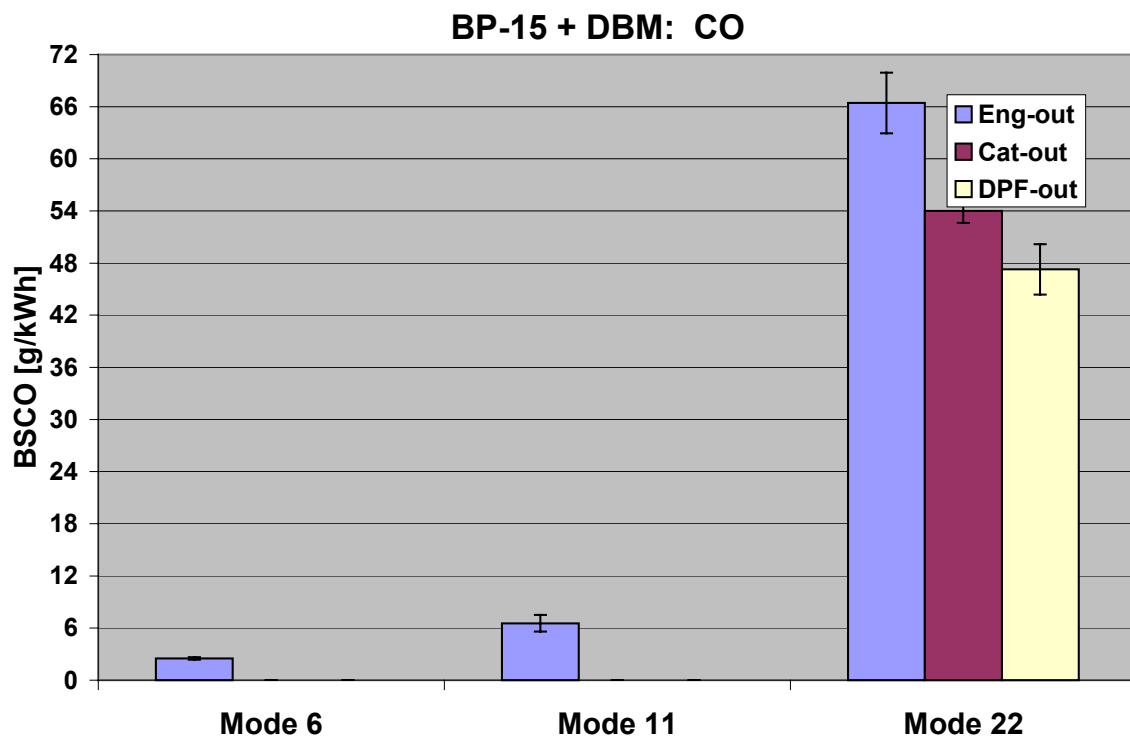


Figure F-8. Carbon Monoxide Emissions with DBM Fuel Additive

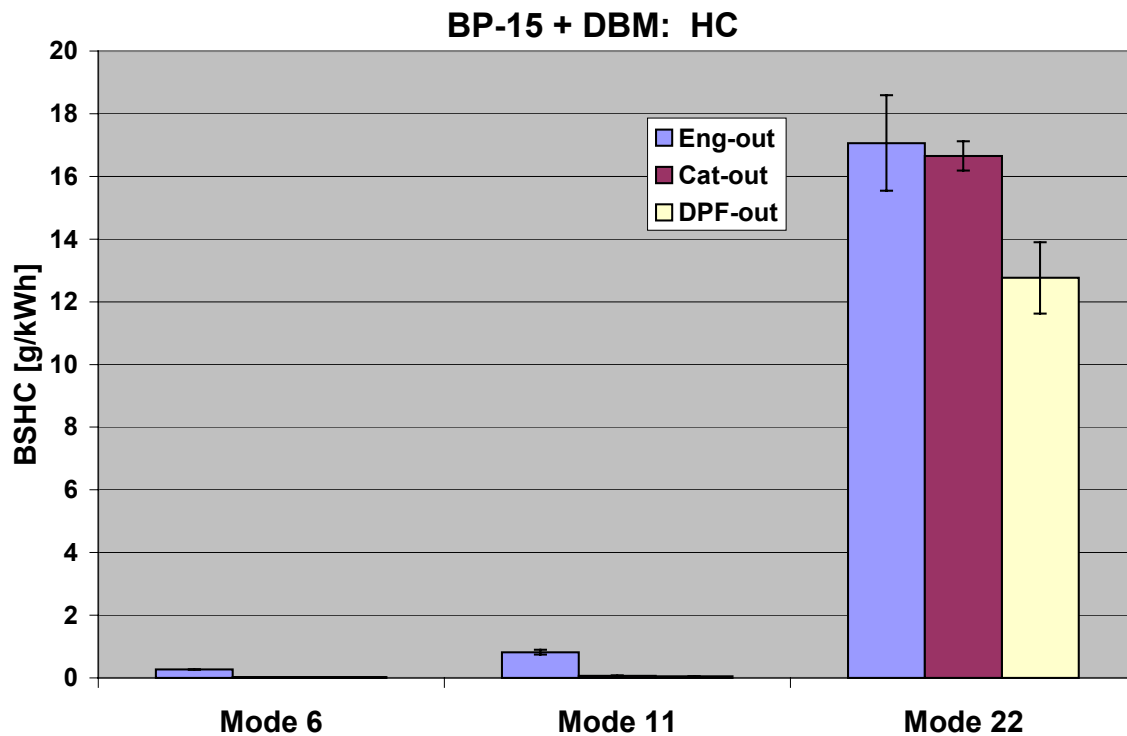


Figure F-9. Hydrocarbon Emissions with DBM Fuel Additive

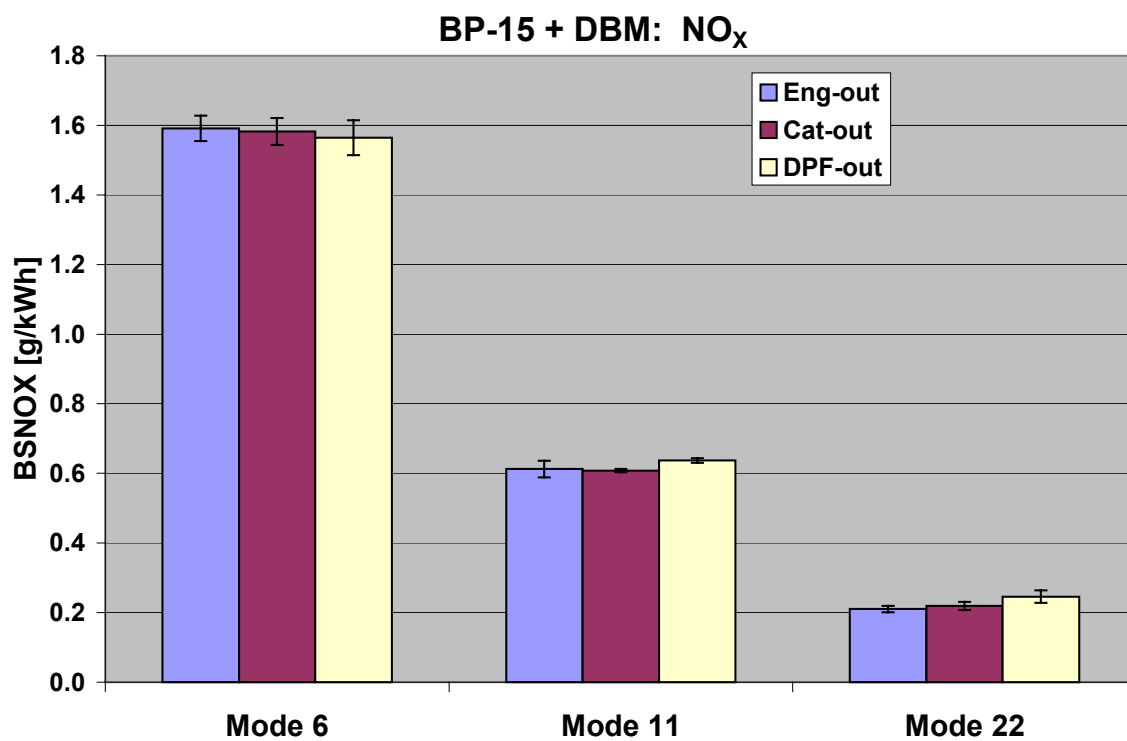


Figure F-10. Nitrogen Oxides Emissions with DBM Fuel Additive

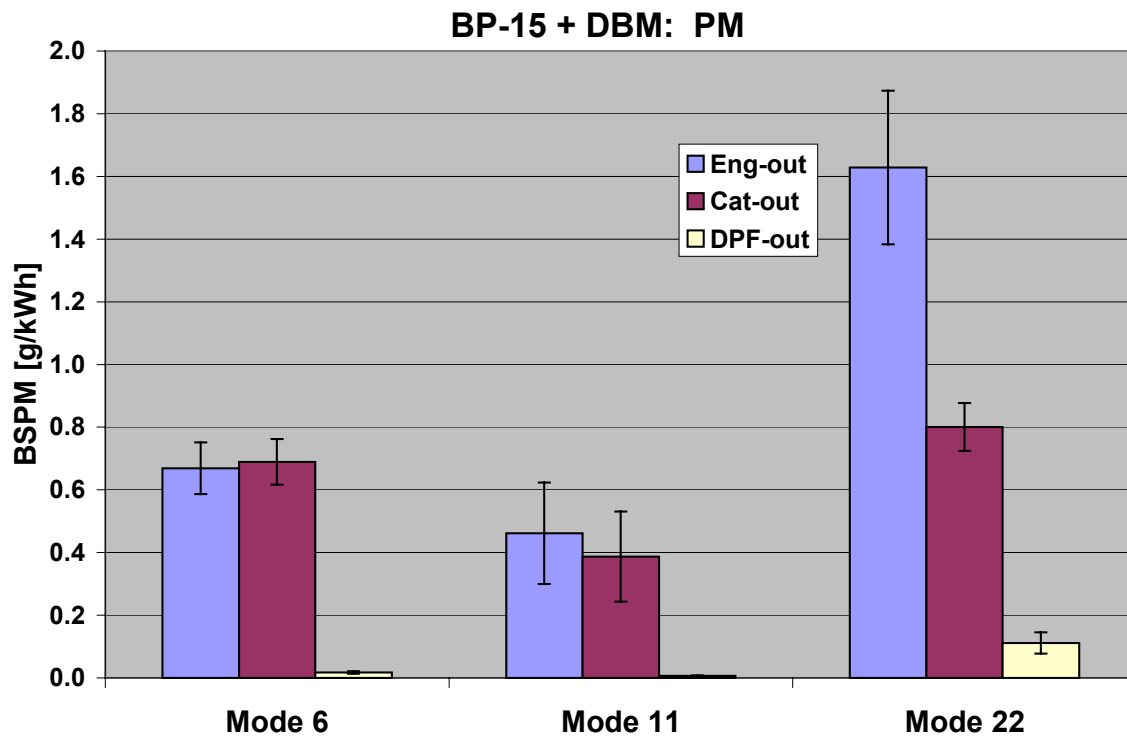


Figure F-11. Particulate Matter Emissions with DBM Fuel Additive

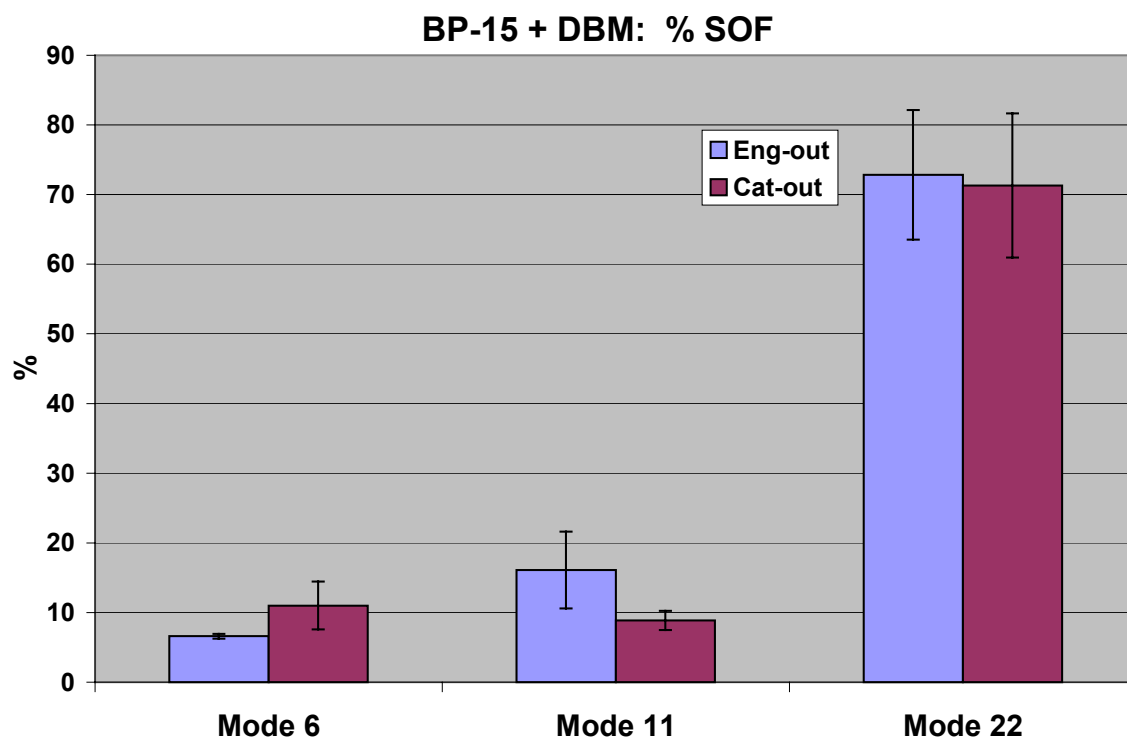


Figure F-12. Percent Soluble Organic Fraction with DBM Fuel Additive

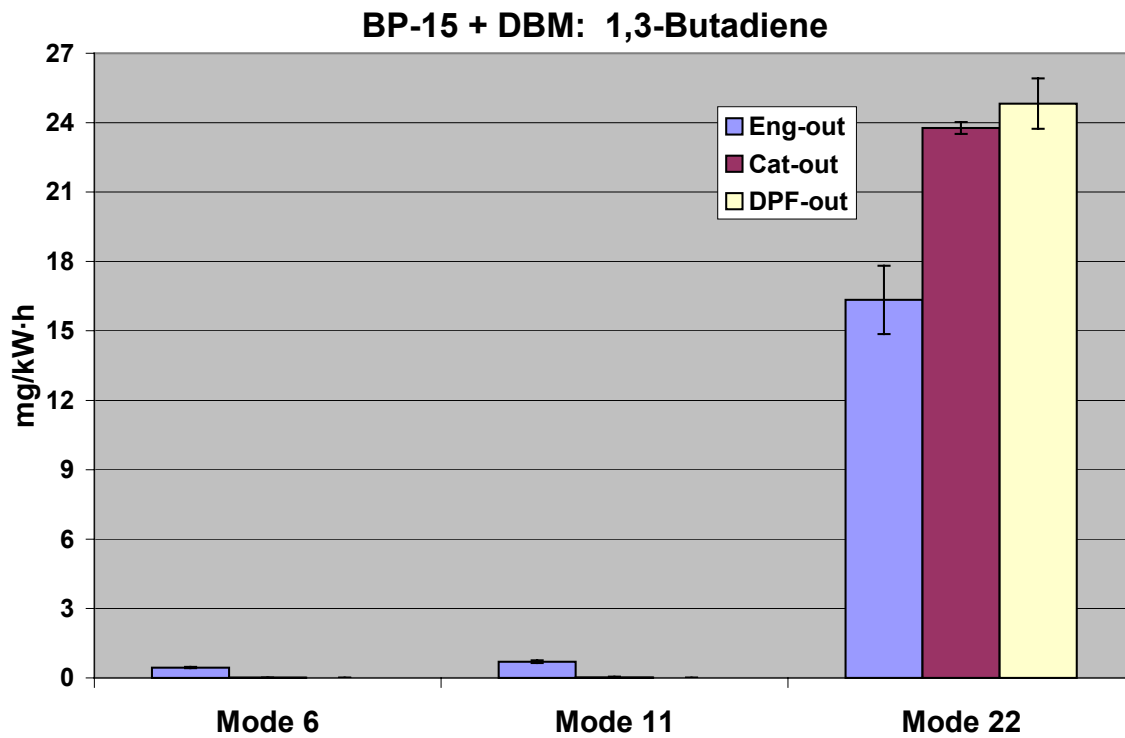


Figure F-13. 1,3-Butadiene Emissions with DBM Fuel Additive

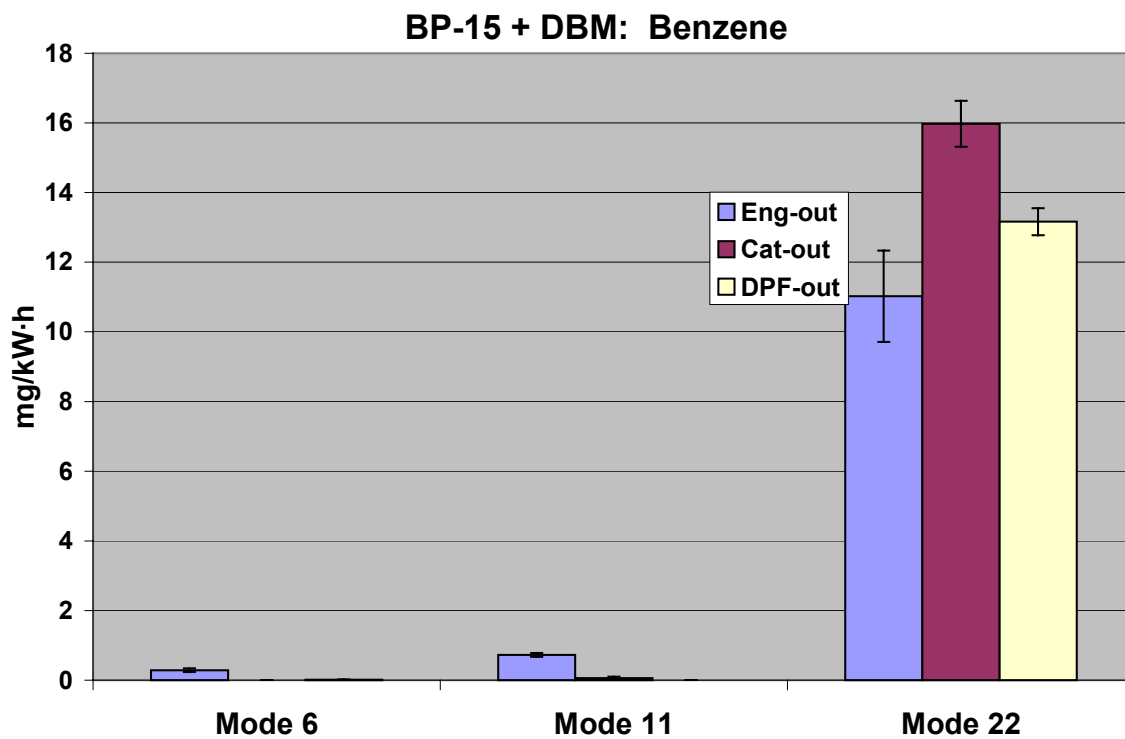


Figure F-14. Benzene Emissions with DBM Fuel Additive

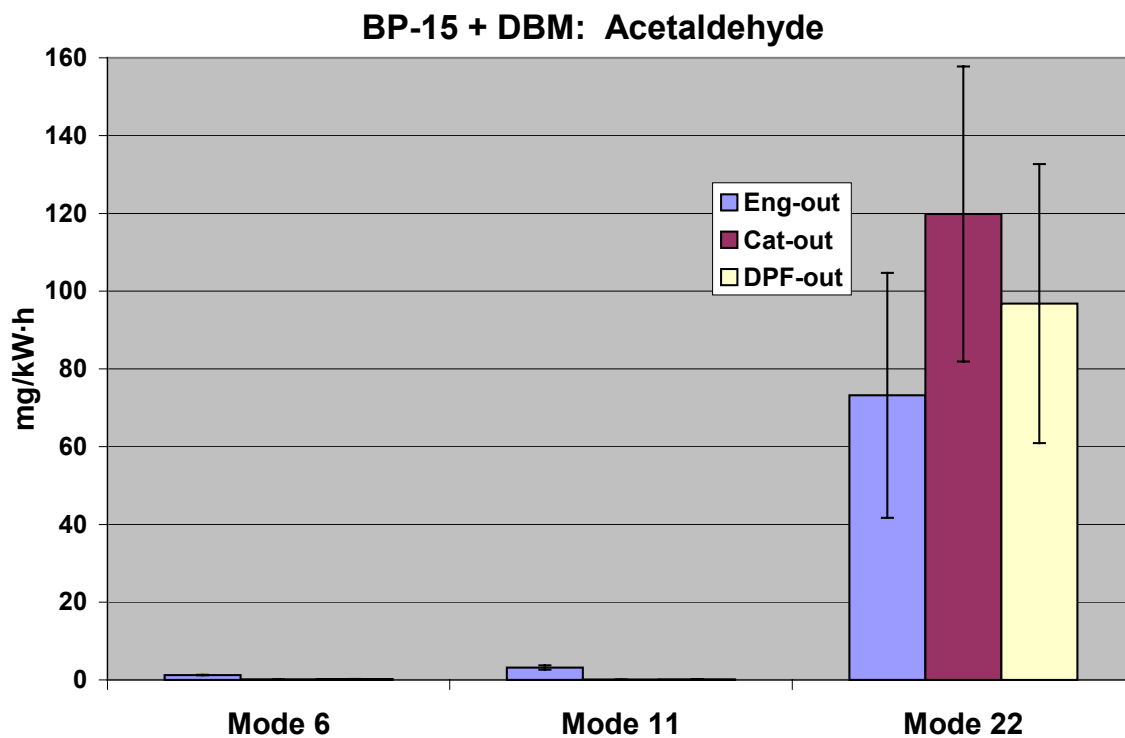


Figure F-15. Acetaldehyde Emissions with DBM Fuel Additive

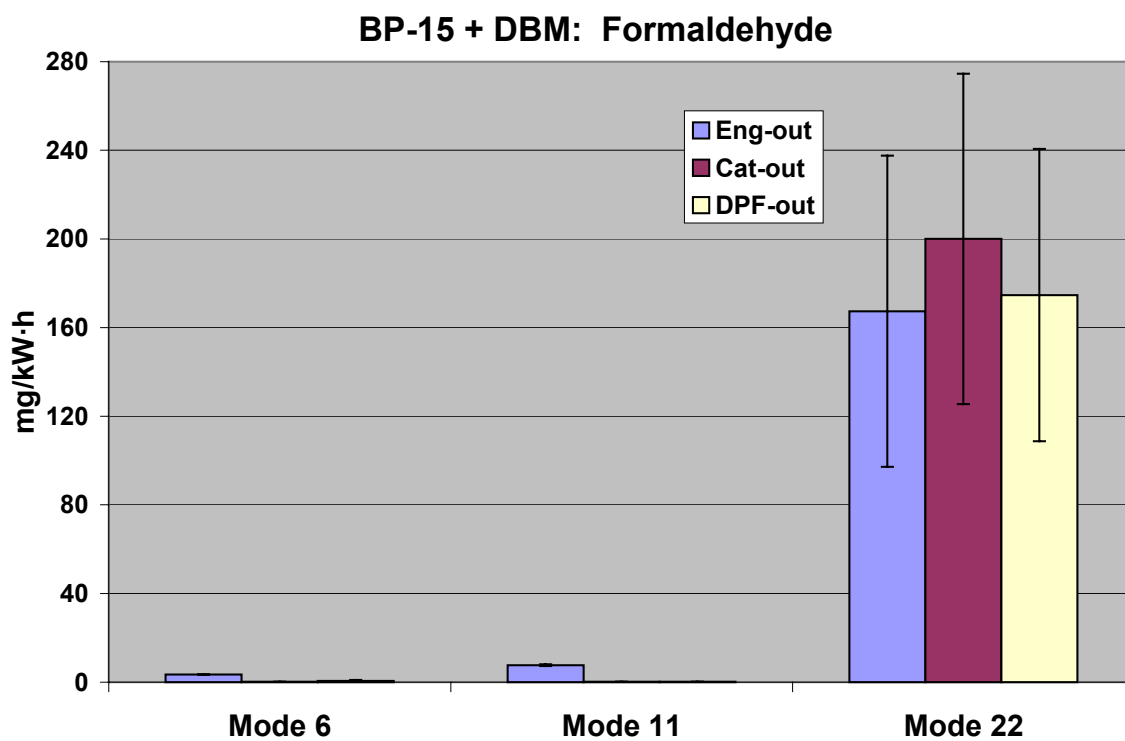


Figure F-16. Formaldehyde Emissions with DBM Fuel Additive



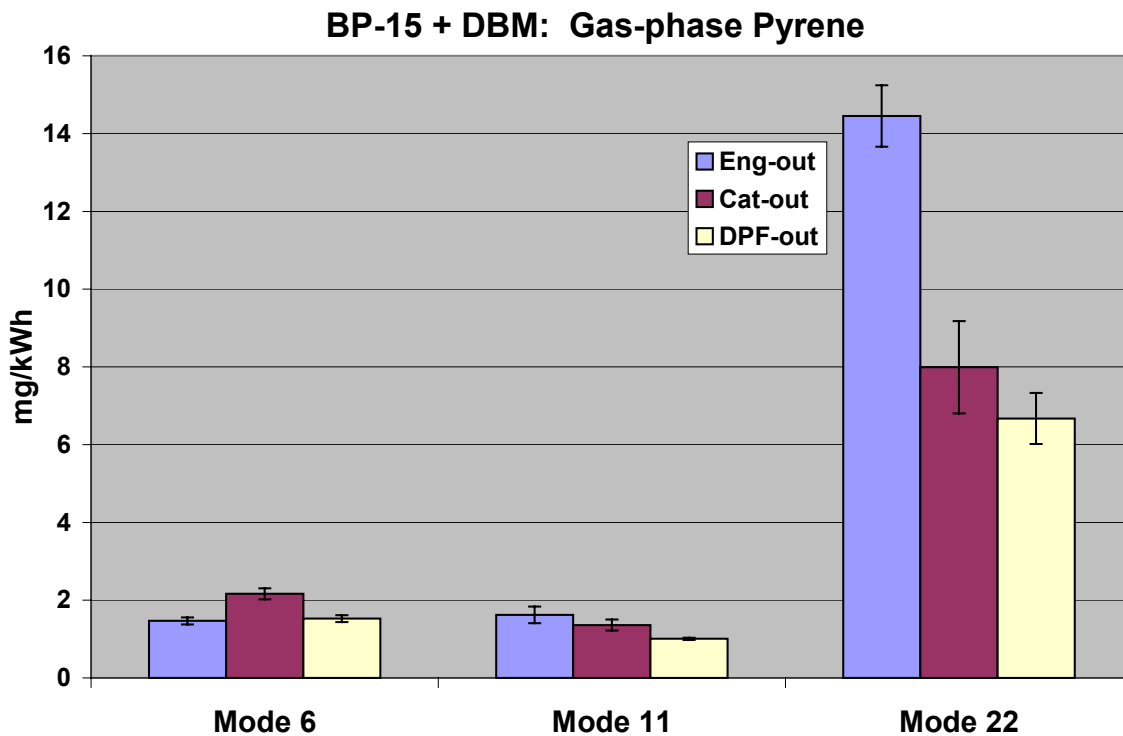


Figure F-17. Gas-Phase Pyrene Emissions with DBM Fuel Additive

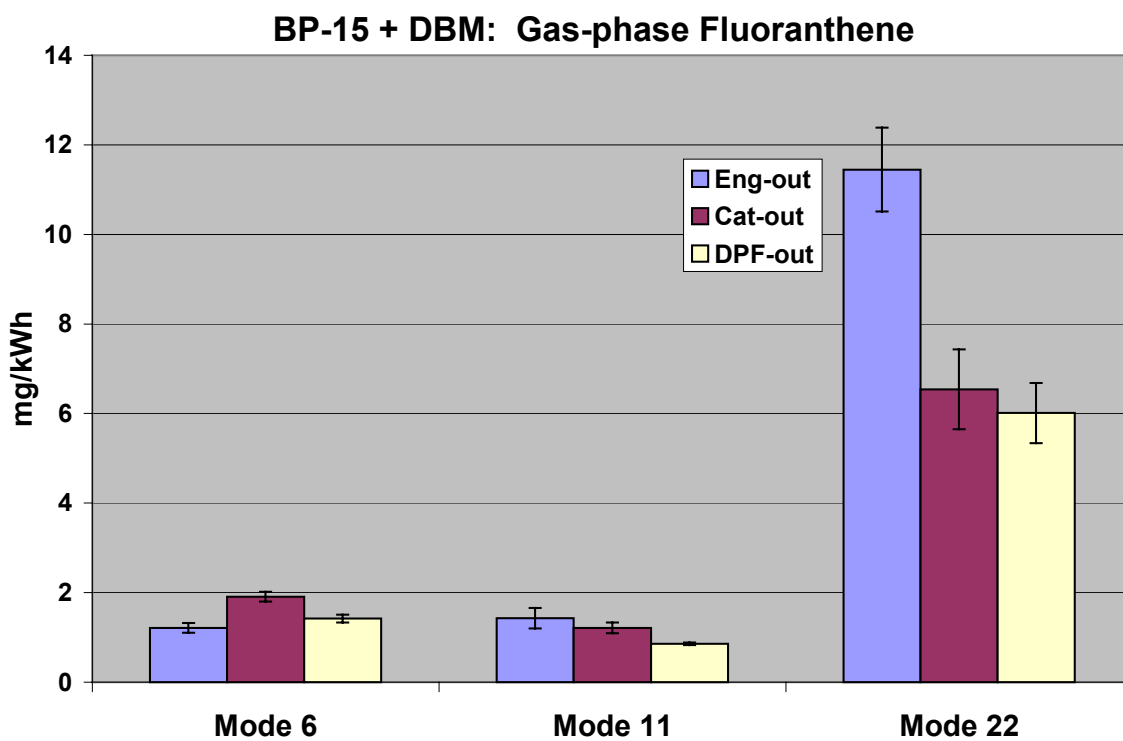


Figure F-18. Gas-Phase Fluoranthene Emissions with DBM Fuel Additive

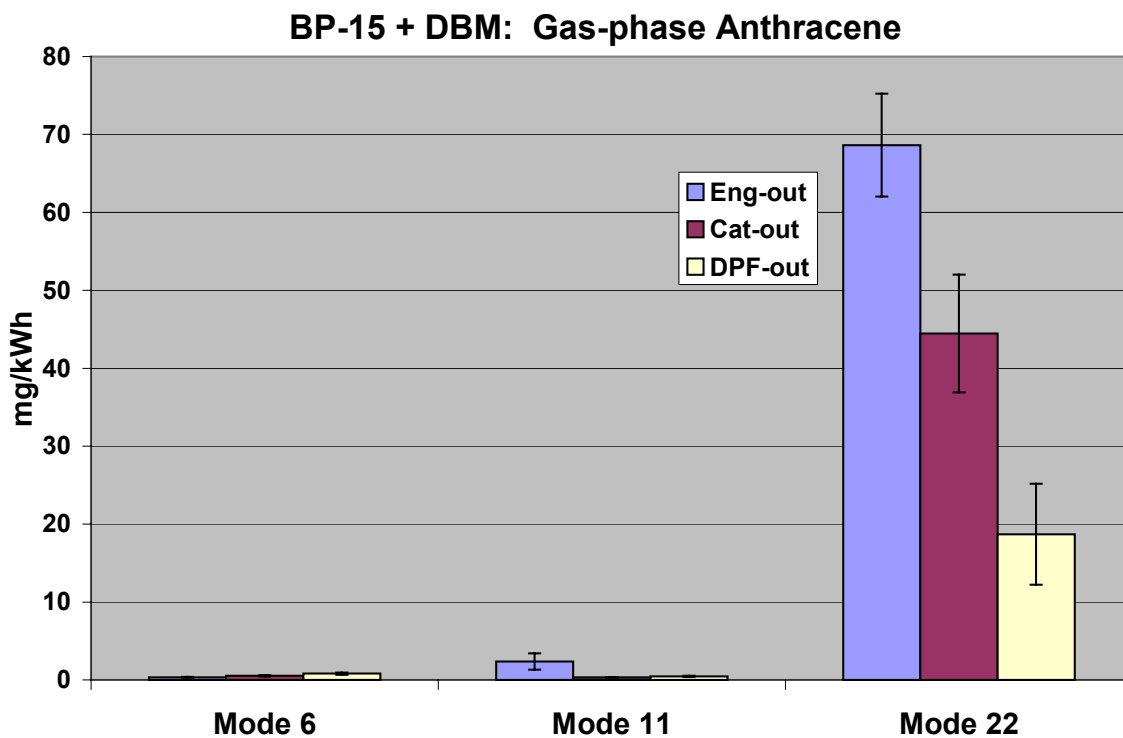


Figure F-19. Gas-Phase Anthracene Emissions with DBM Fuel Additive

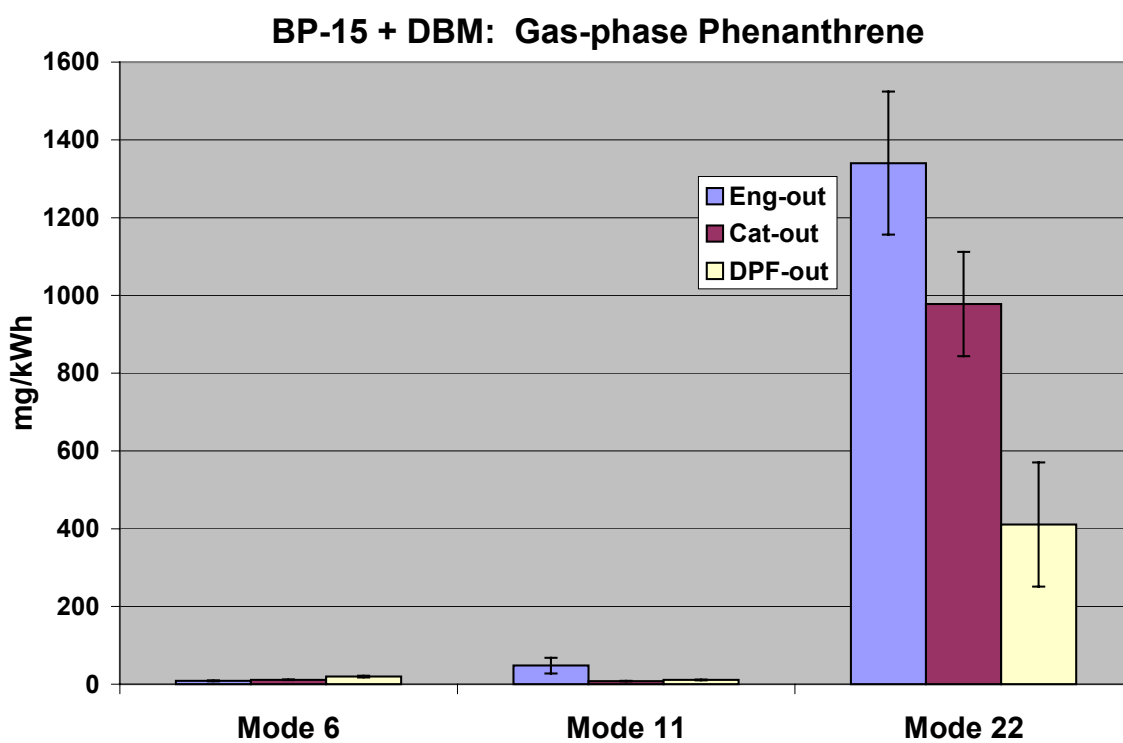


Figure F-20. Gas-Phase Phenanthrene Emissions with DBM Fuel Additive

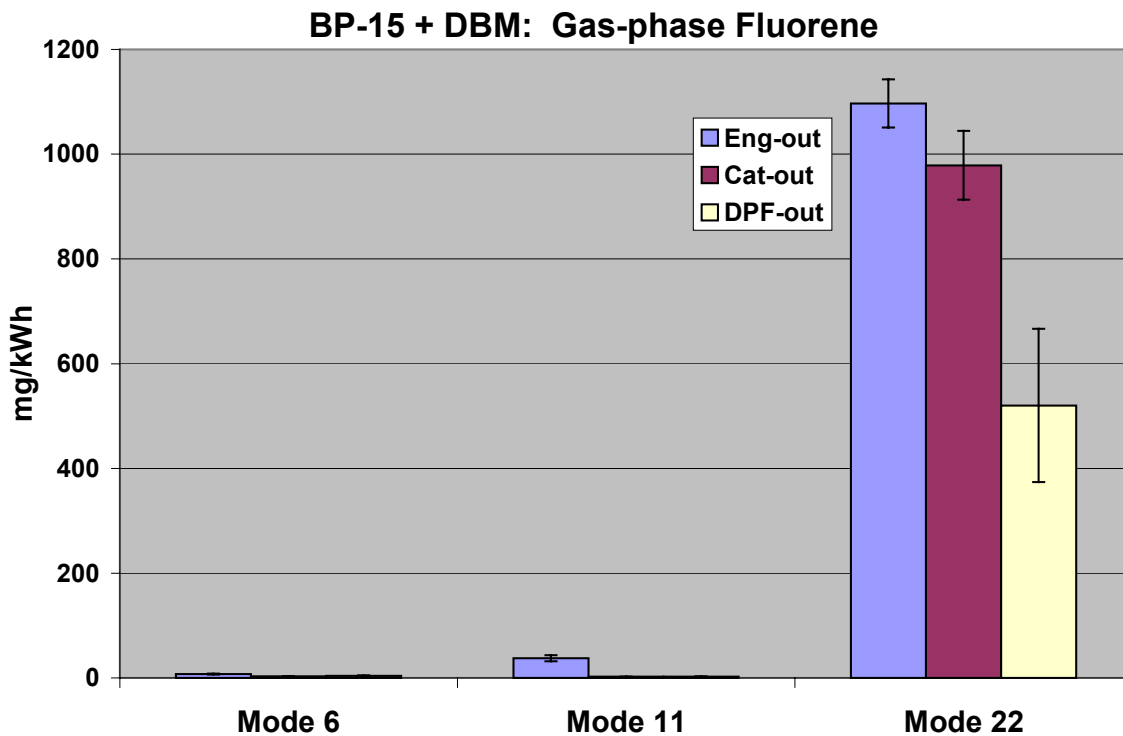


Figure F-21. Gas-Phase Fluorene Emissions with DBM Fuel Additive

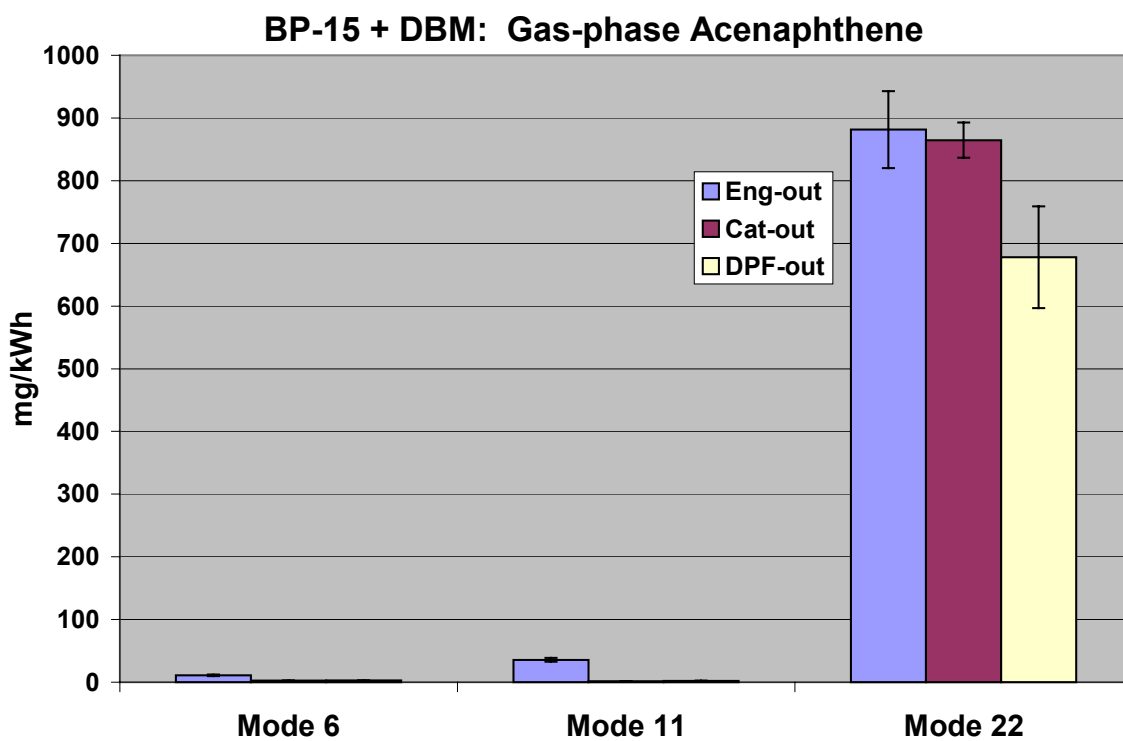


Figure F-22. Gas-Phase Acenaphthene Emissions with DBM Fuel Additive

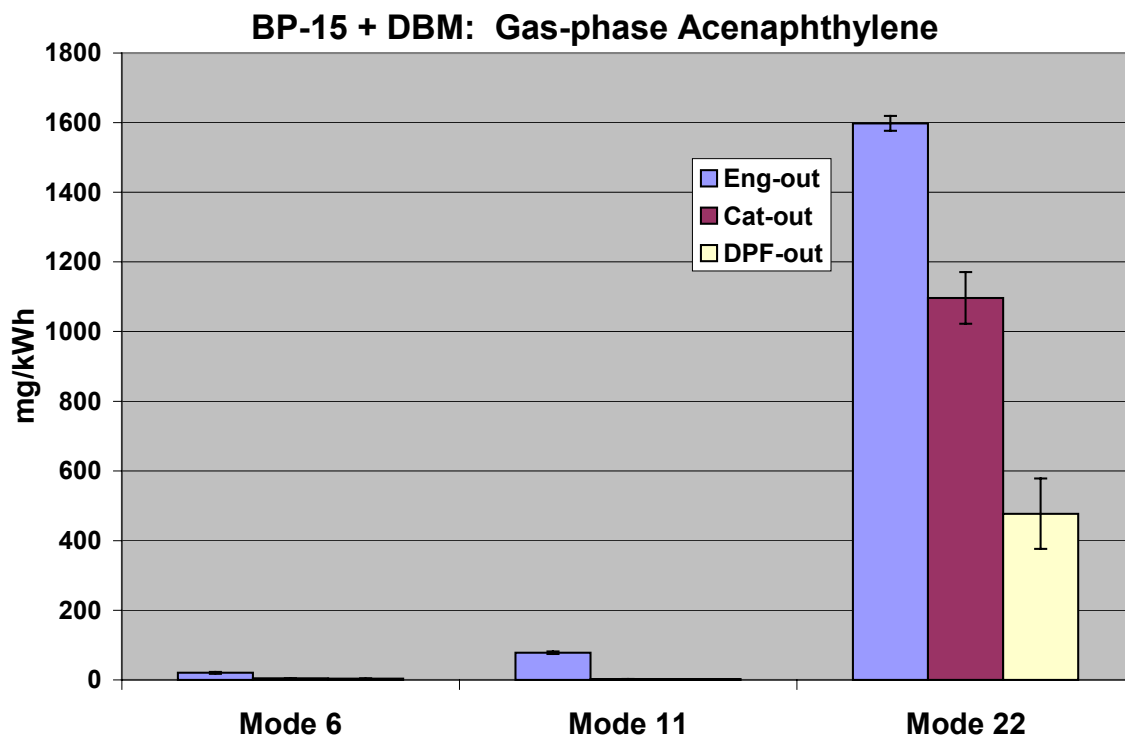


Figure F-23. Gas-Phase Acenaphthylene Emissions with DBM Fuel Additive

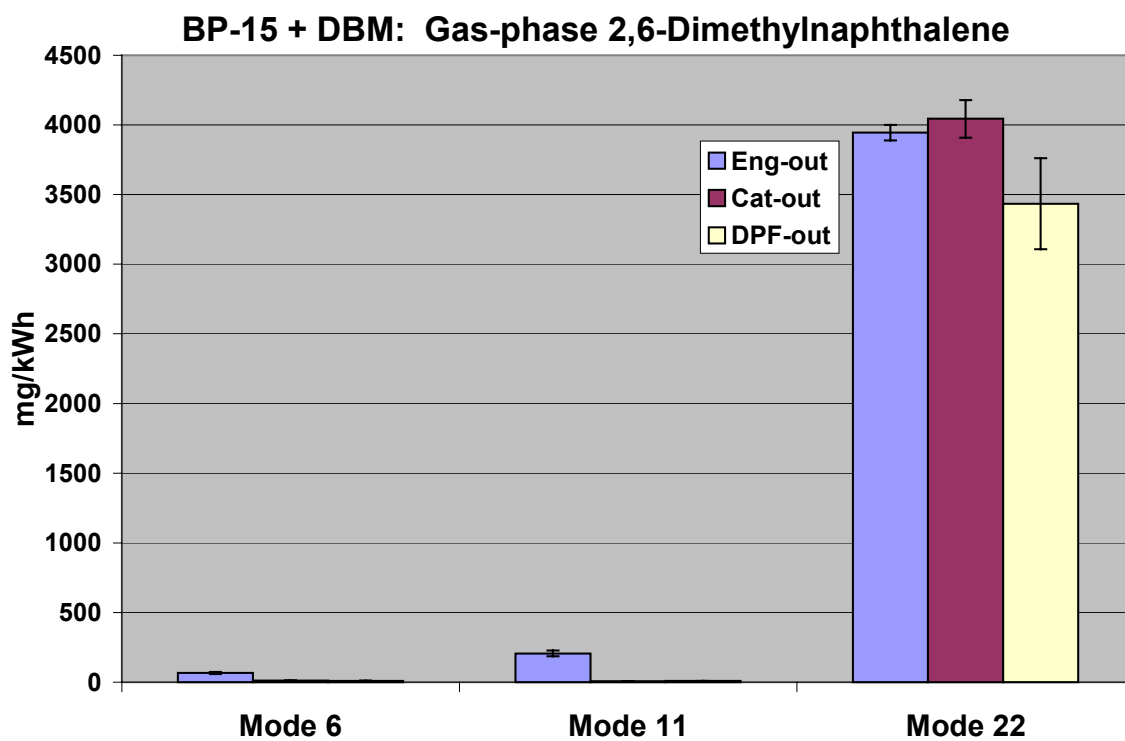


Figure F-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions with DBM Fuel Additive

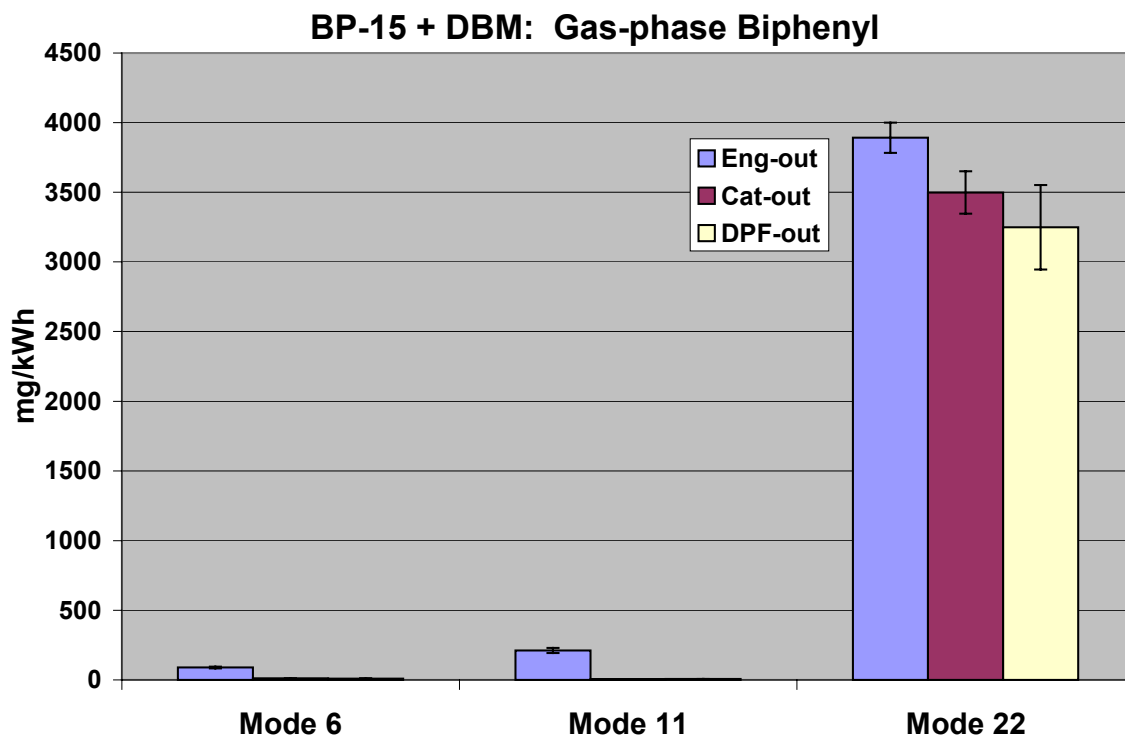


Figure F-25. Gas-Phase Biphenyl Emissions with DBM Fuel Additive

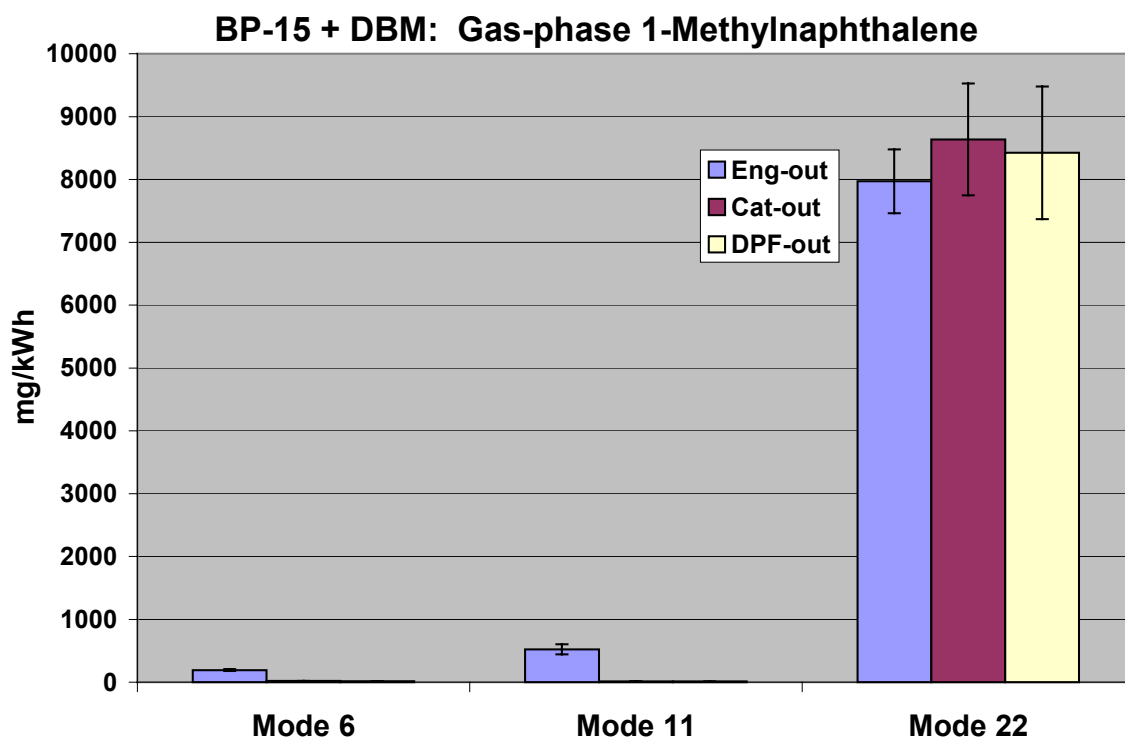


Figure F-26. Gas-Phase 1-Methylnaphthalene Emissions with DBM Fuel Additive

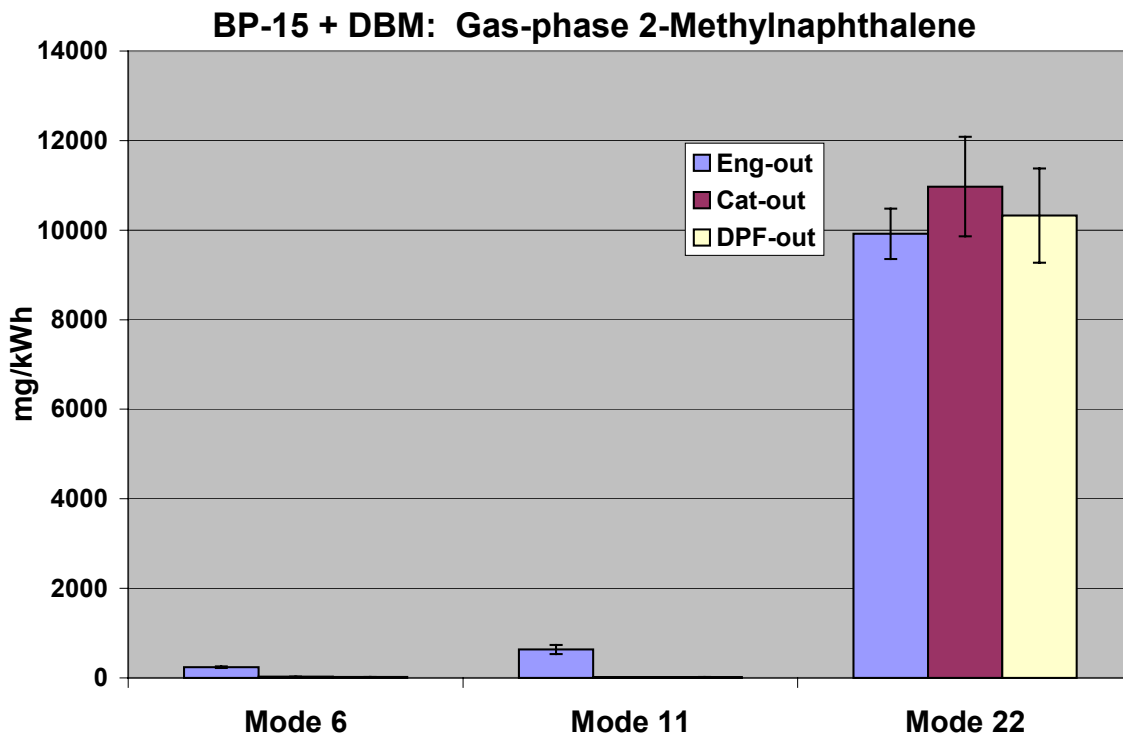


Figure F-27. Gas-Phase 2-Methylnaphthalene Emissions with DBM Fuel Additive

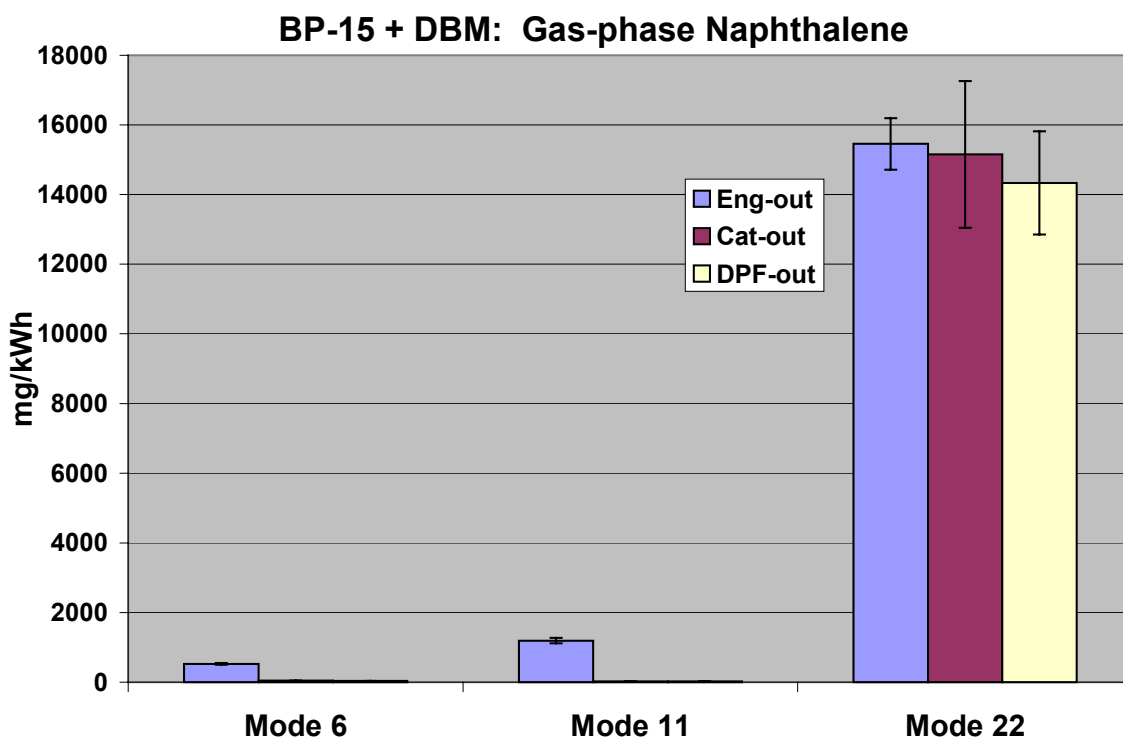


Figure F-28. Gas-Phase Naphthalene Emissions with DBM Fuel Additive

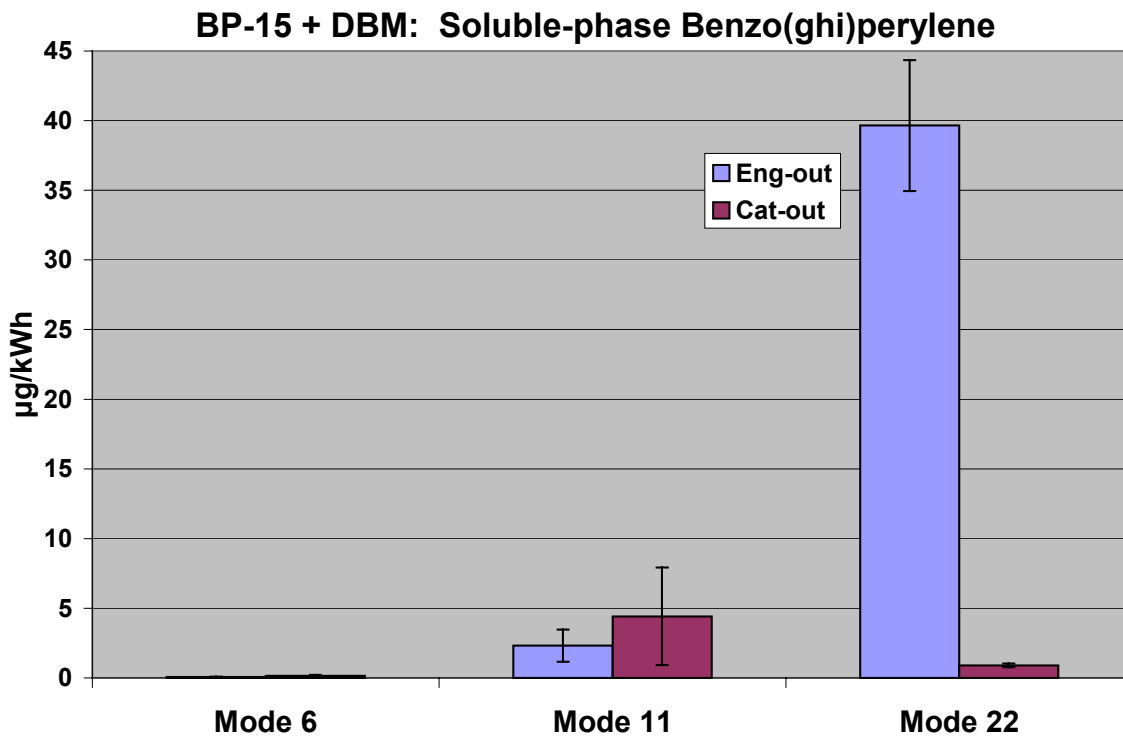


Figure F-29. Soluble-Phase Benzo(ghi)perylene Emissions with DBM Fuel Additive

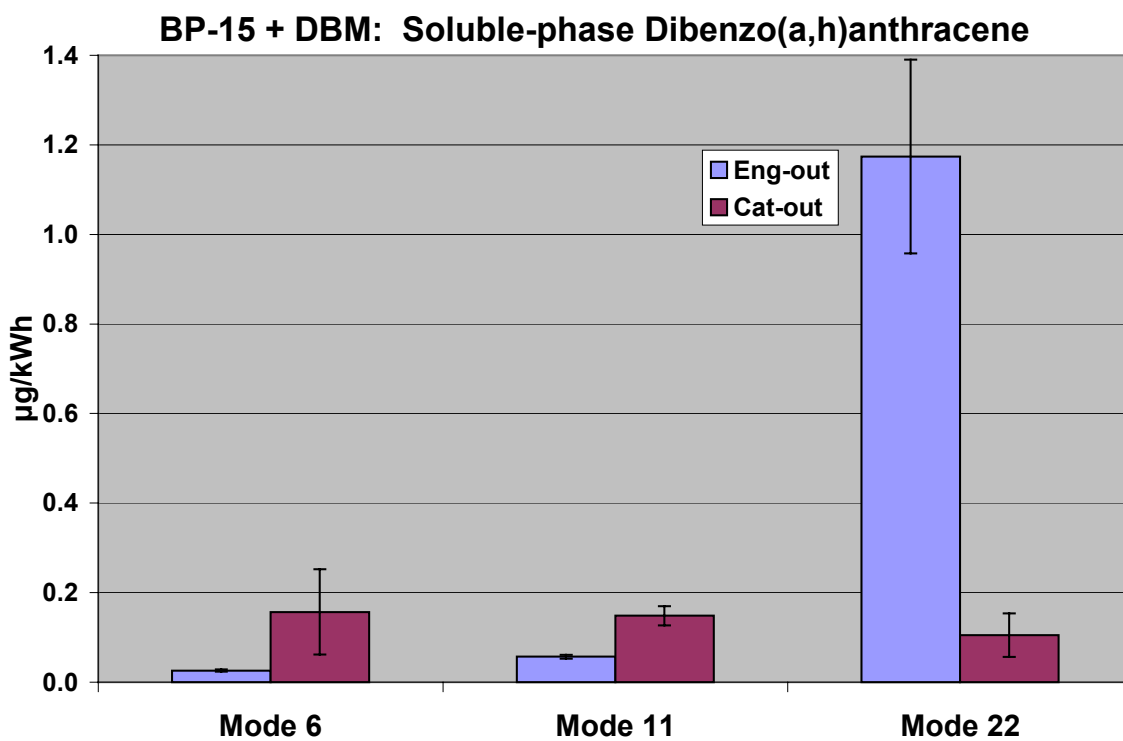


Figure F-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions with DBM Fuel Additive

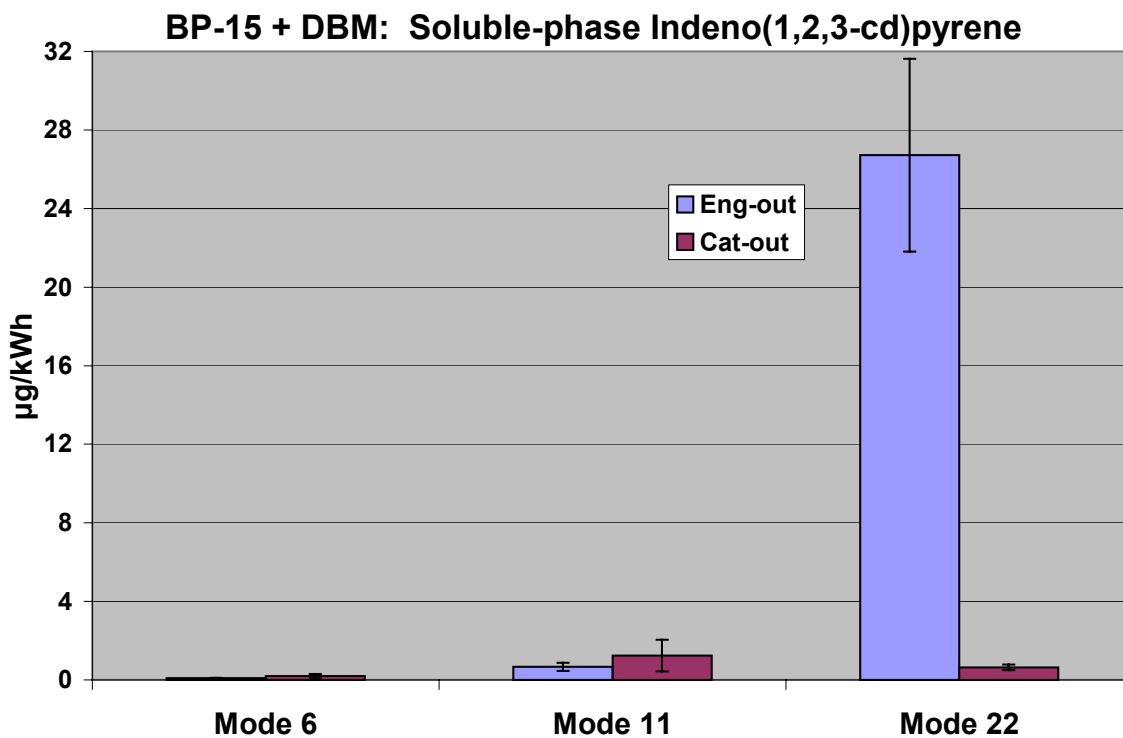


Figure F-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions with DBM Fuel Additive

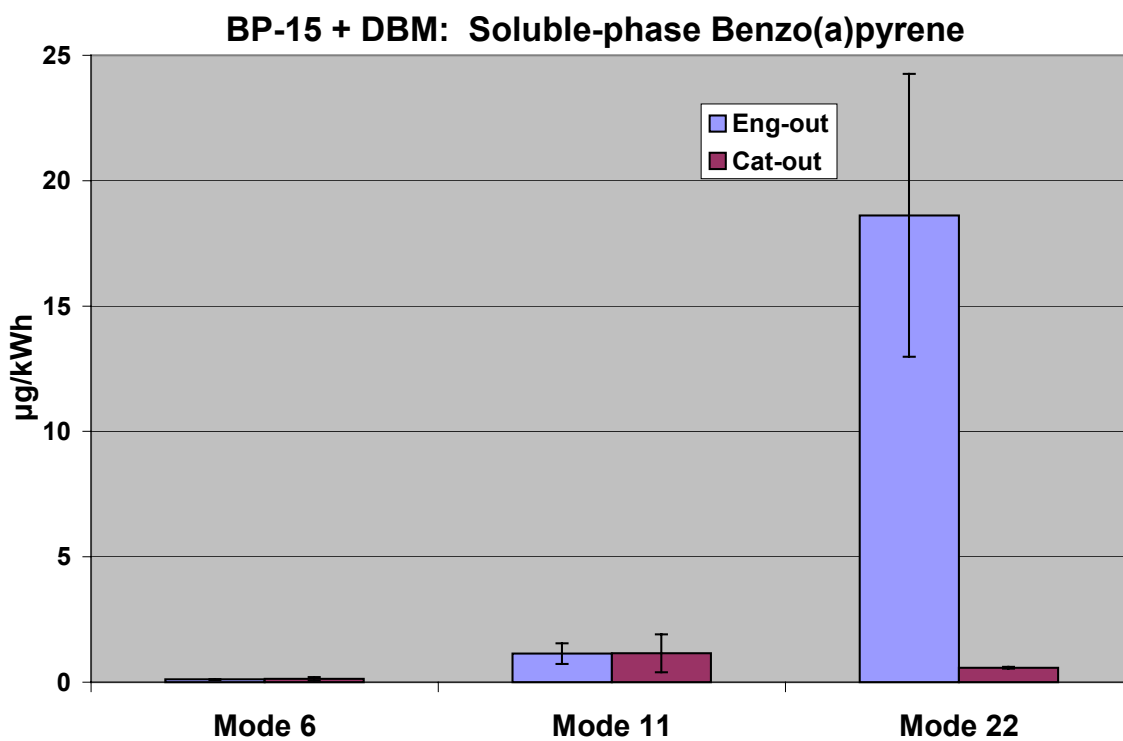


Figure F-32. Soluble-Phase Benzo(a)pyrene Emissions with DBM Fuel Additive



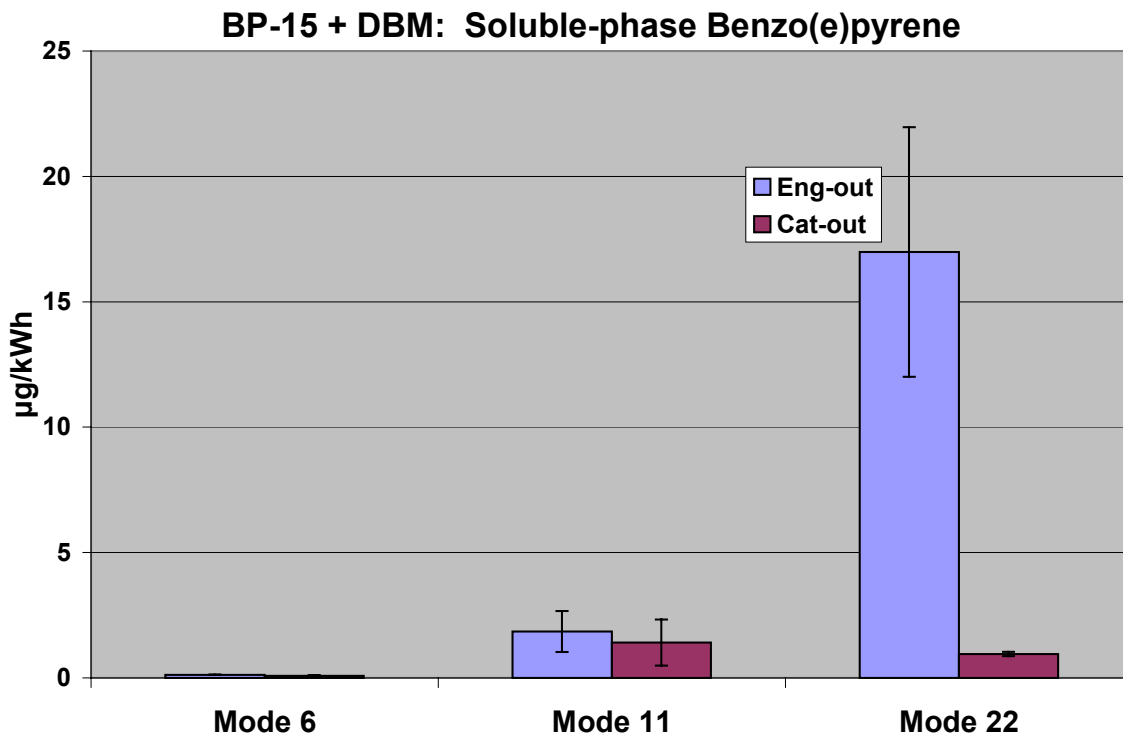


Figure F-33. Soluble-Phase Benzo(e)pyrene Emissions with DBM Fuel Additive

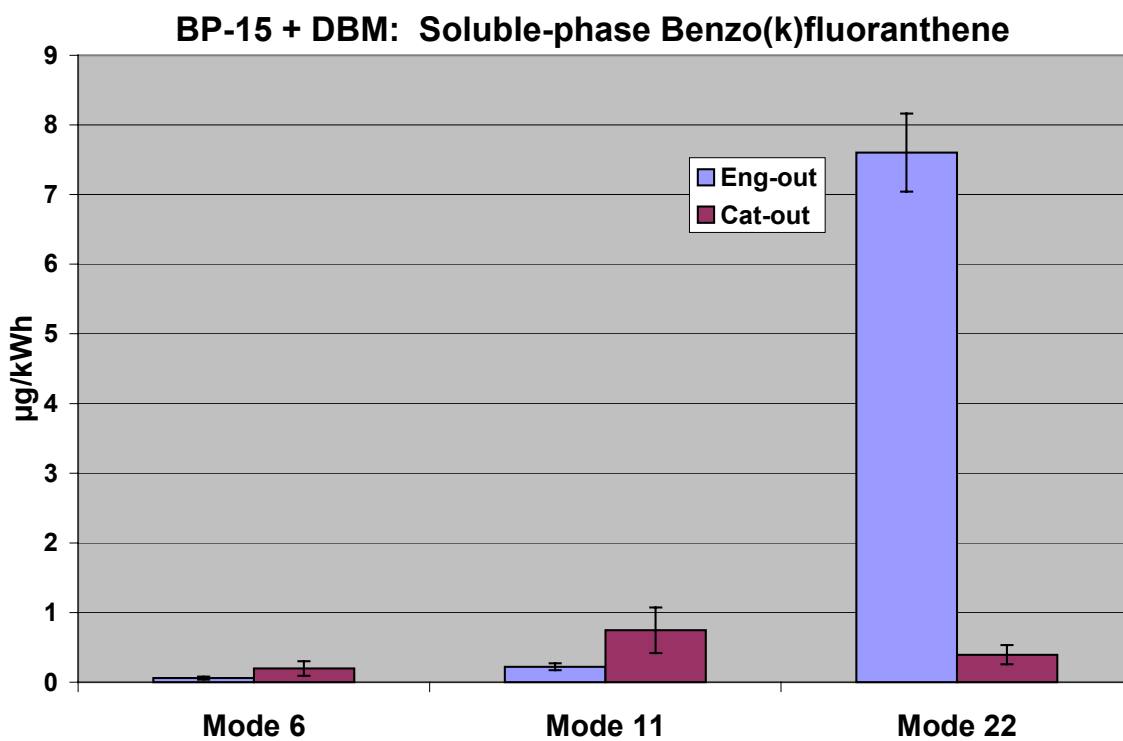


Figure F-34. Soluble-Phase Benzo(k)fluoranthene Emissions with DBM Fuel Additive

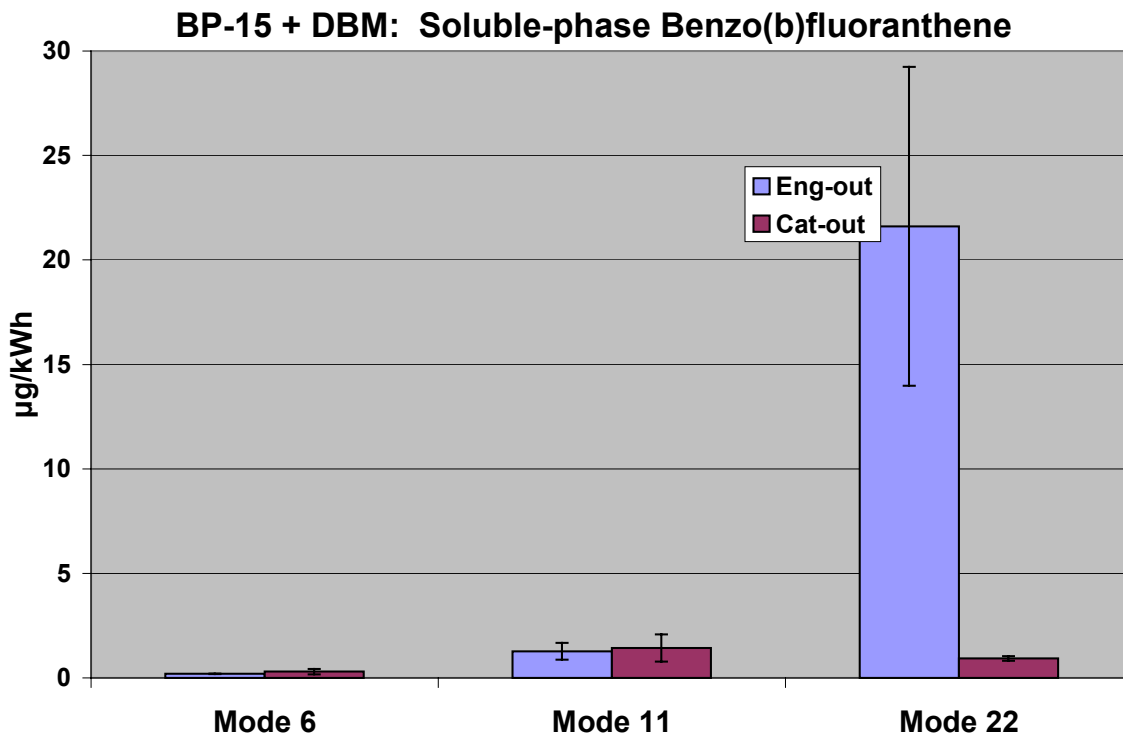


Figure F-35. Soluble-Phase Benzo(b)fluoranthene Emissions with DBM Fuel Additive

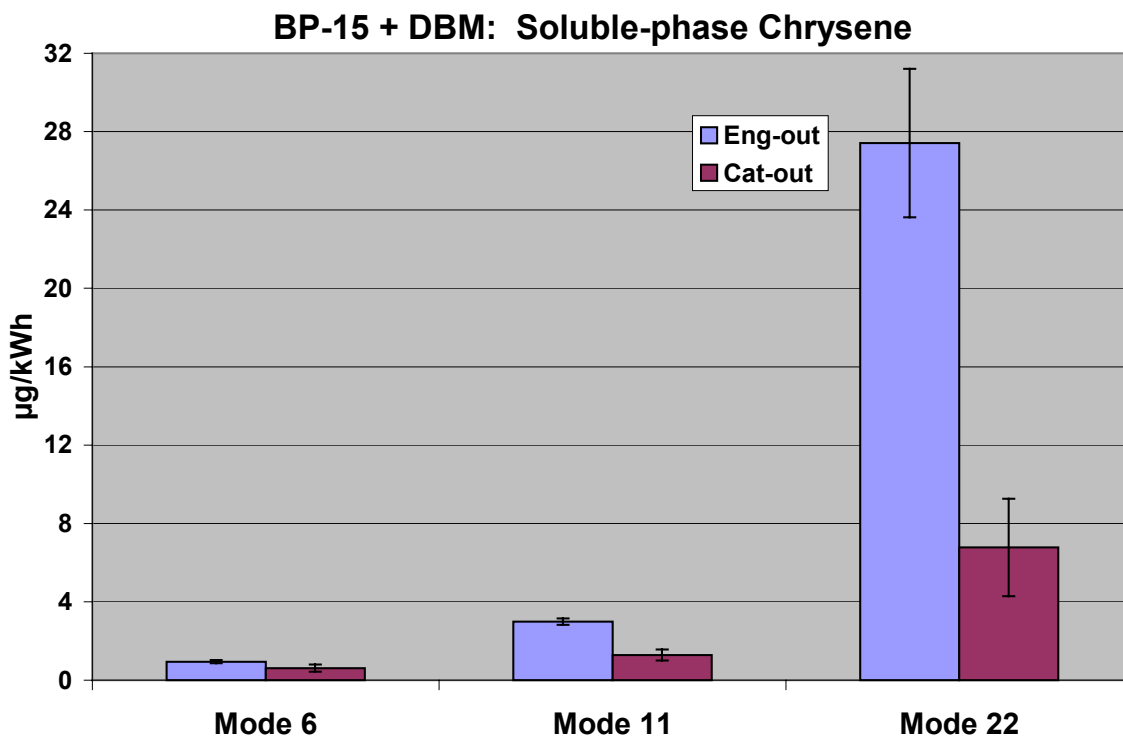


Figure F-36. Soluble-Phase Chrysene Emissions with DBM Fuel Additive

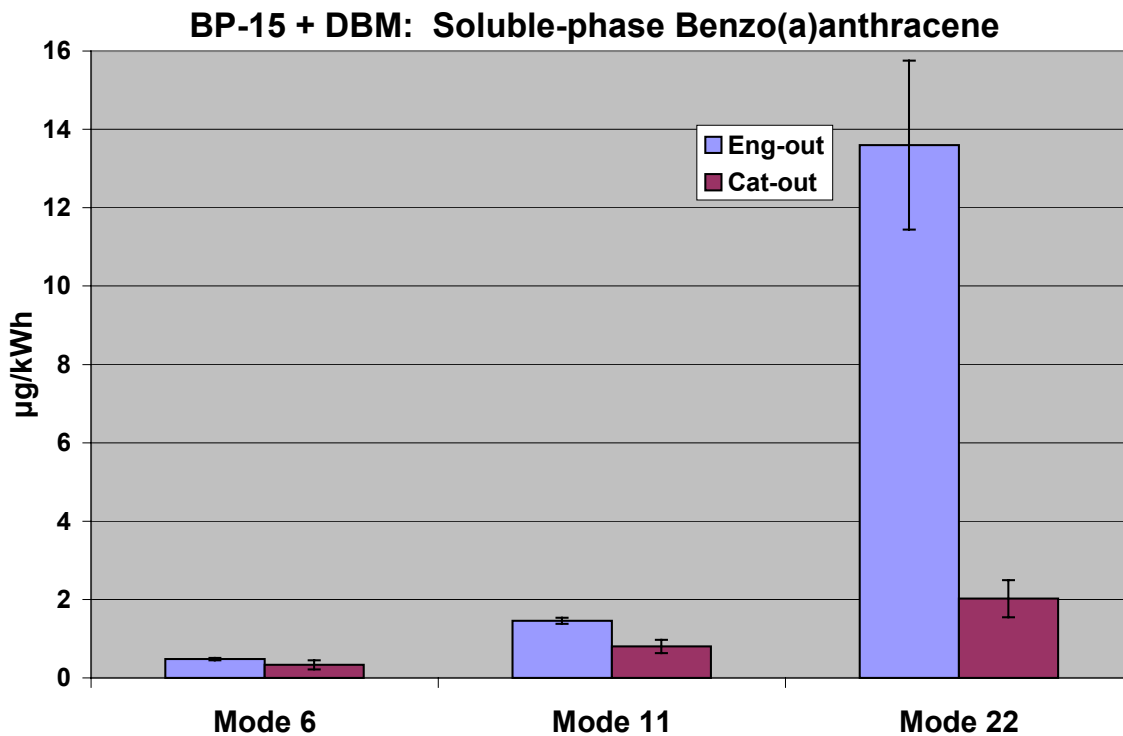


Figure F-37. Soluble-Phase Benzo(a)anthracene Emissions with DBM Fuel Additive

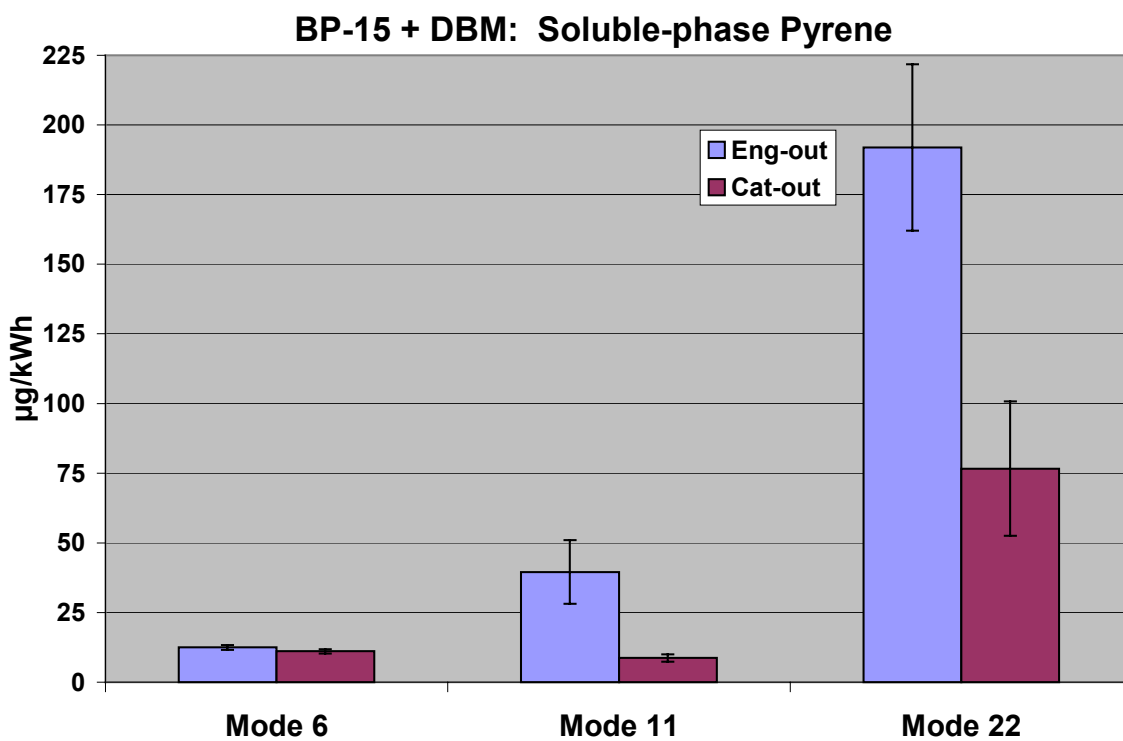


Figure F-38. Soluble-Phase Pyrene Emissions with DBM Fuel Additive

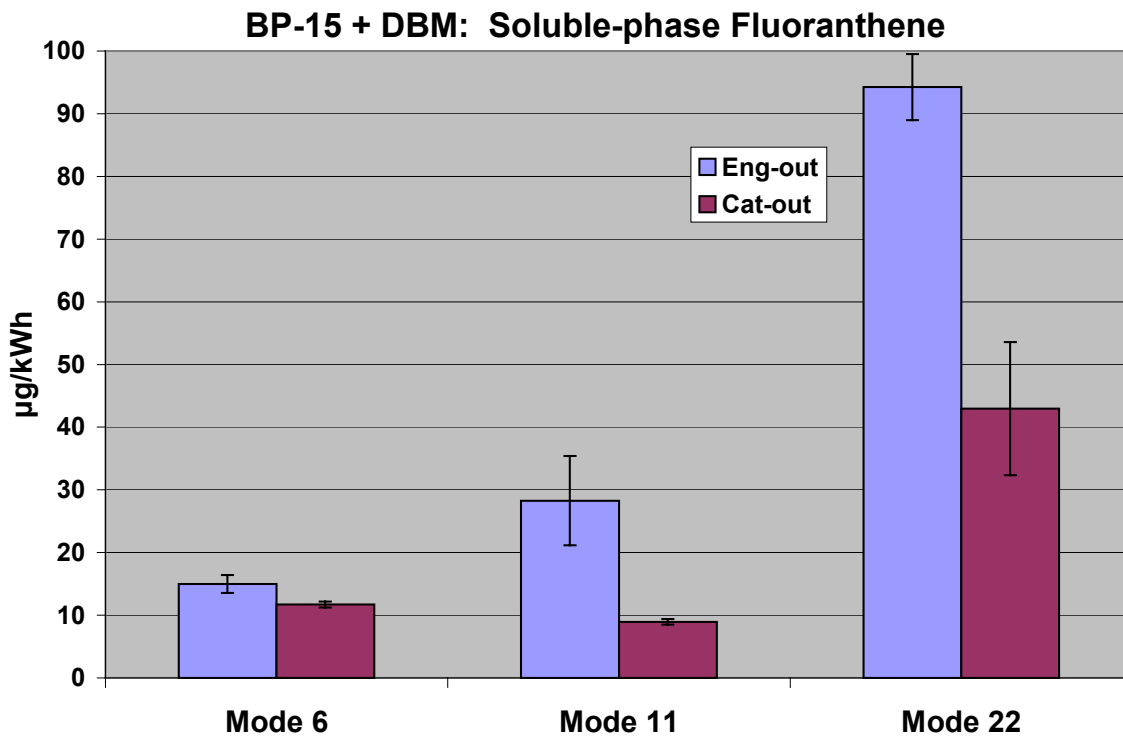


Figure F-39. Soluble-Phase Fluoranthene Emissions with DBM Fuel Additive

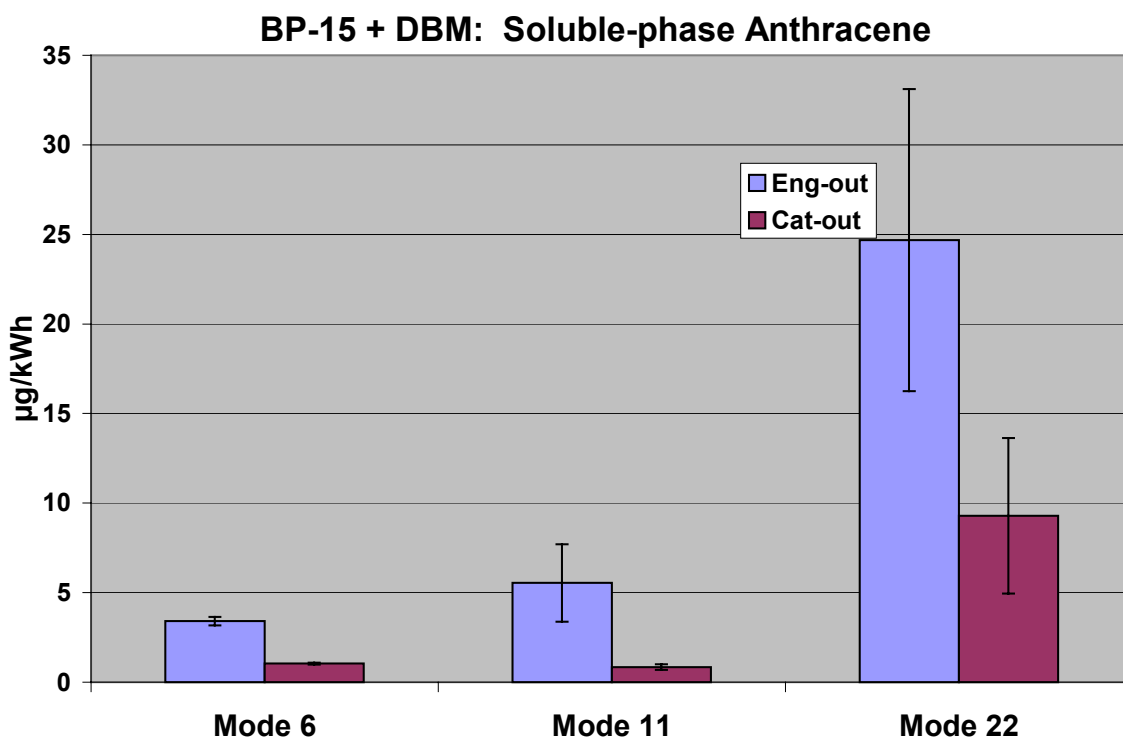


Figure F-40. Soluble-Phase Anthracene Emissions with DBM Fuel Additive

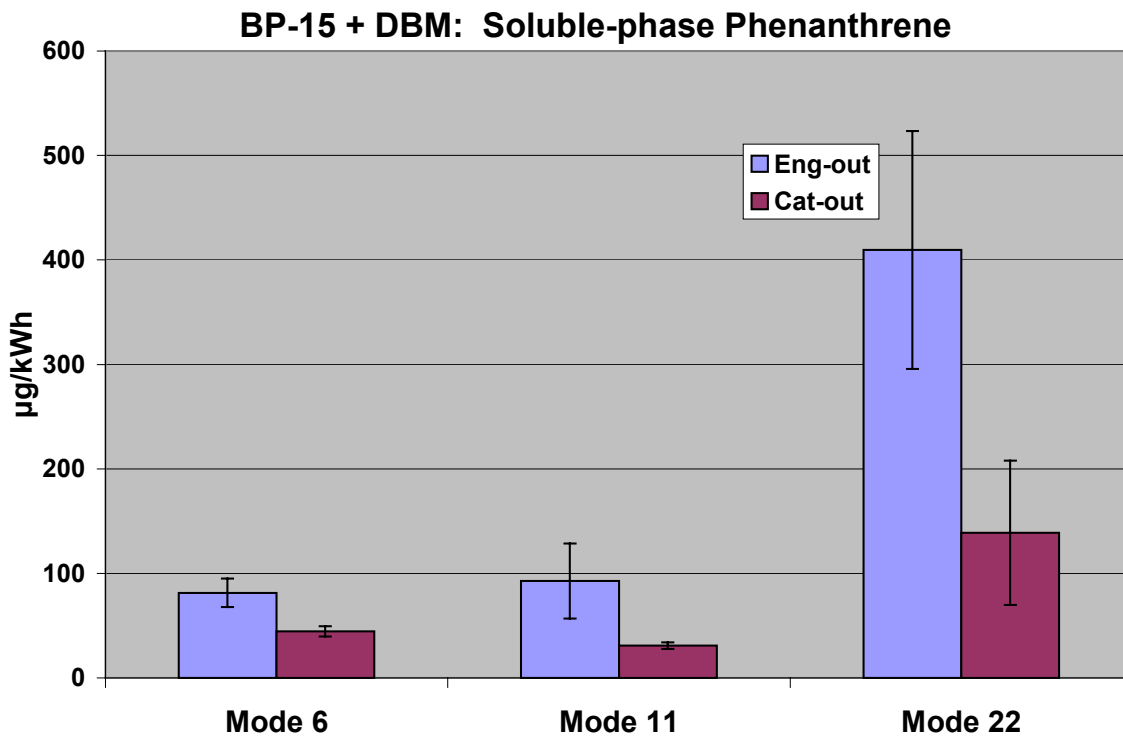


Figure F-41. Soluble-Phase Phenanthrene Emissions with DBM Fuel Additive

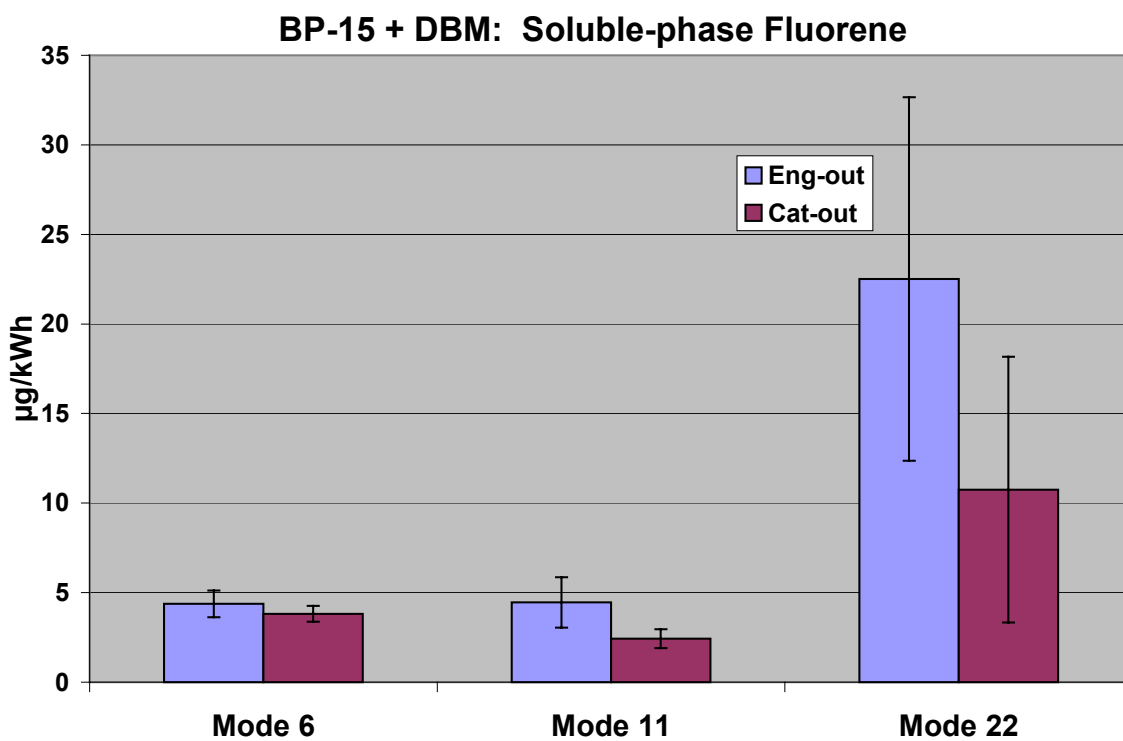


Figure F-42. Soluble-Phase Fluorene Emissions with DBM Fuel Additive

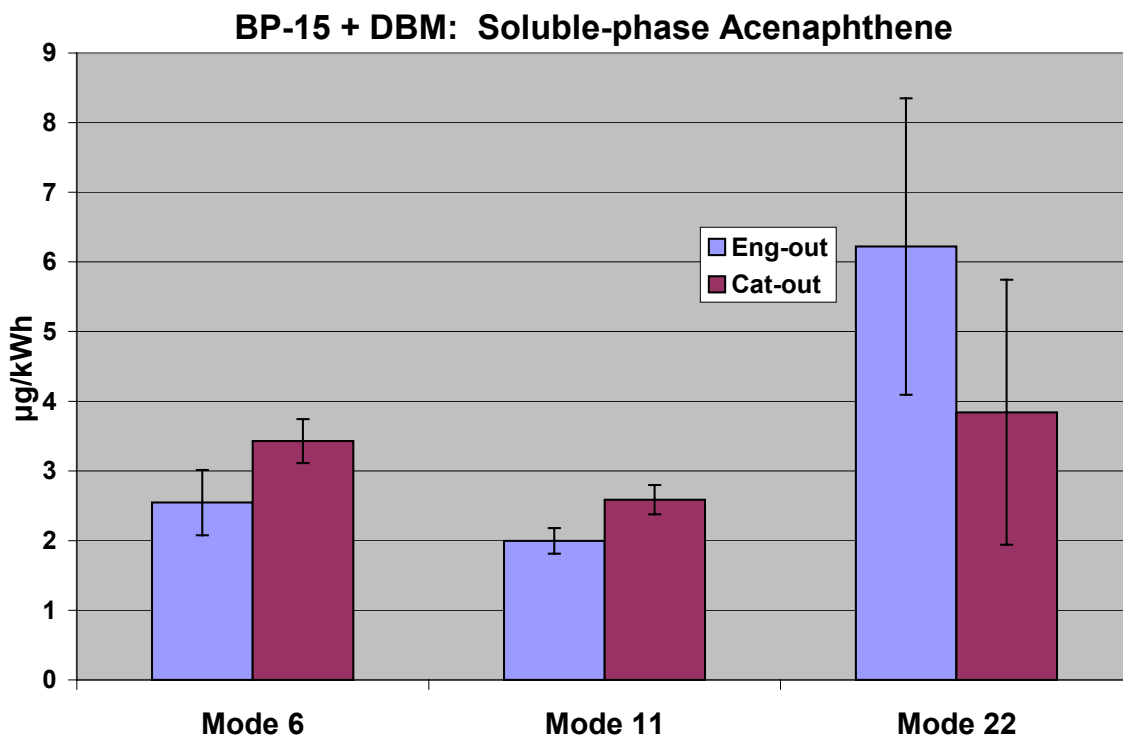


Figure F-43. Soluble-Phase Acenaphthene Emissions with DBM Fuel Additive

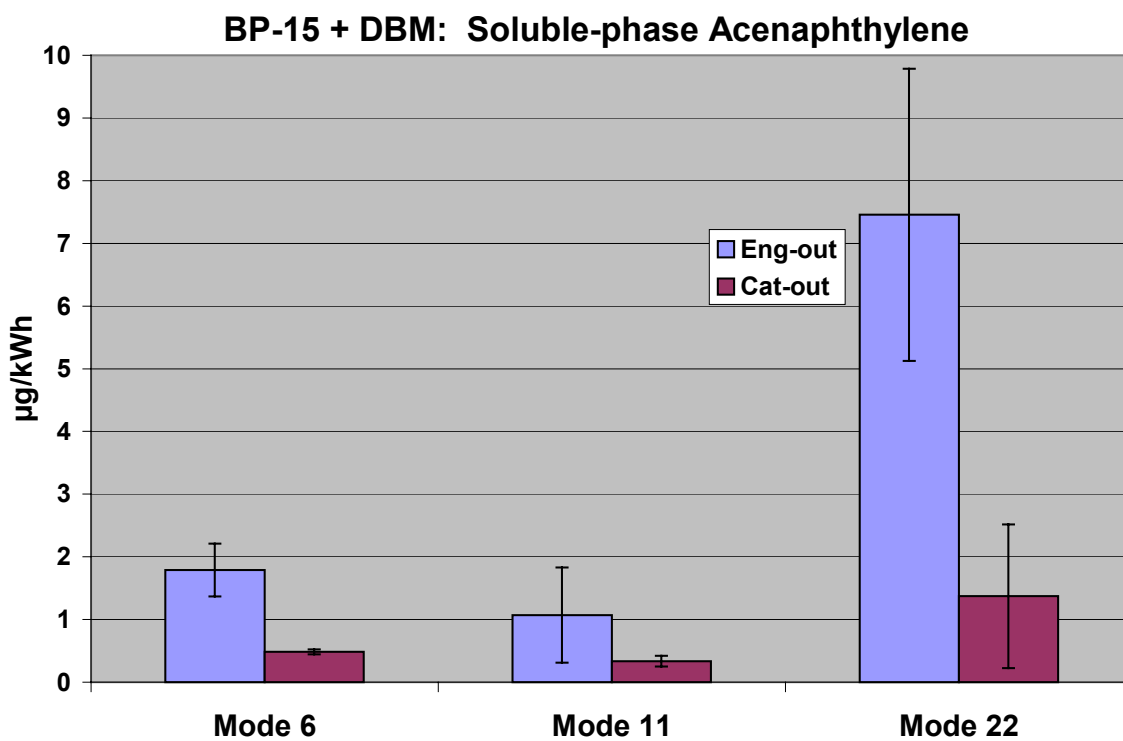


Figure F-44. Soluble-Phase Acenaphthylene Emissions with DBM Fuel Additive

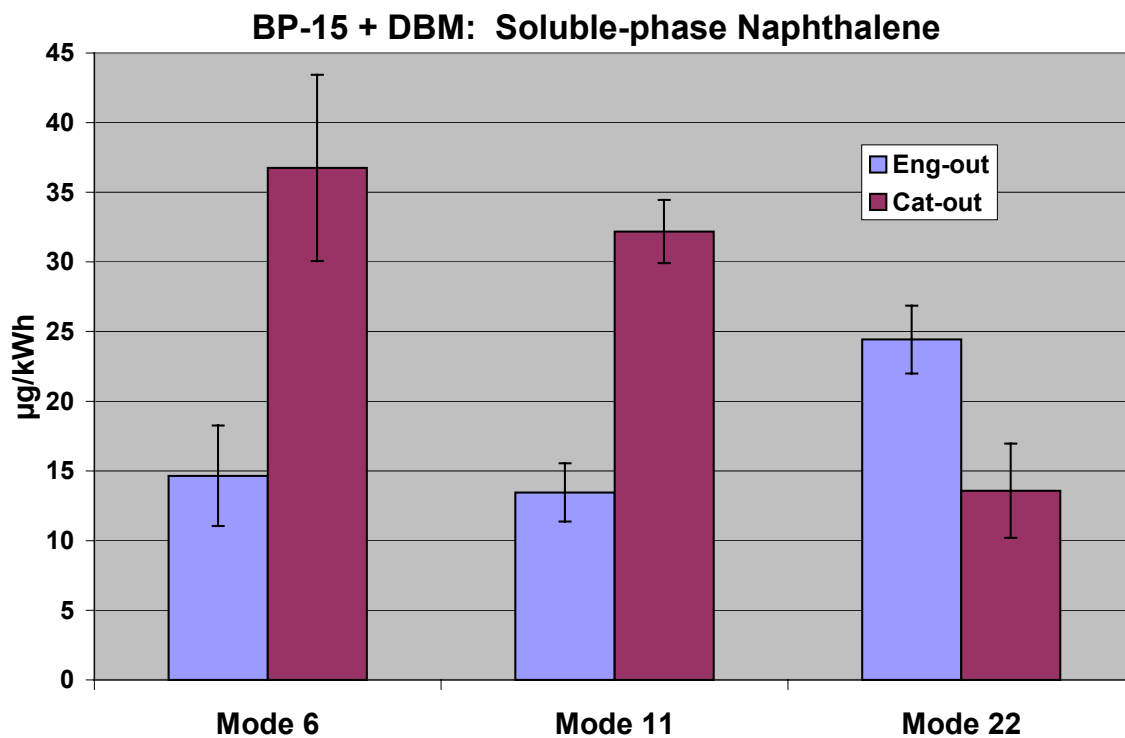


Figure F-45. Soluble-Phase Naphthalene Emissions with DBM Fuel Additive

## **APPENDIX G**

### **BP15+TPGME Fuel Operation Test Results**



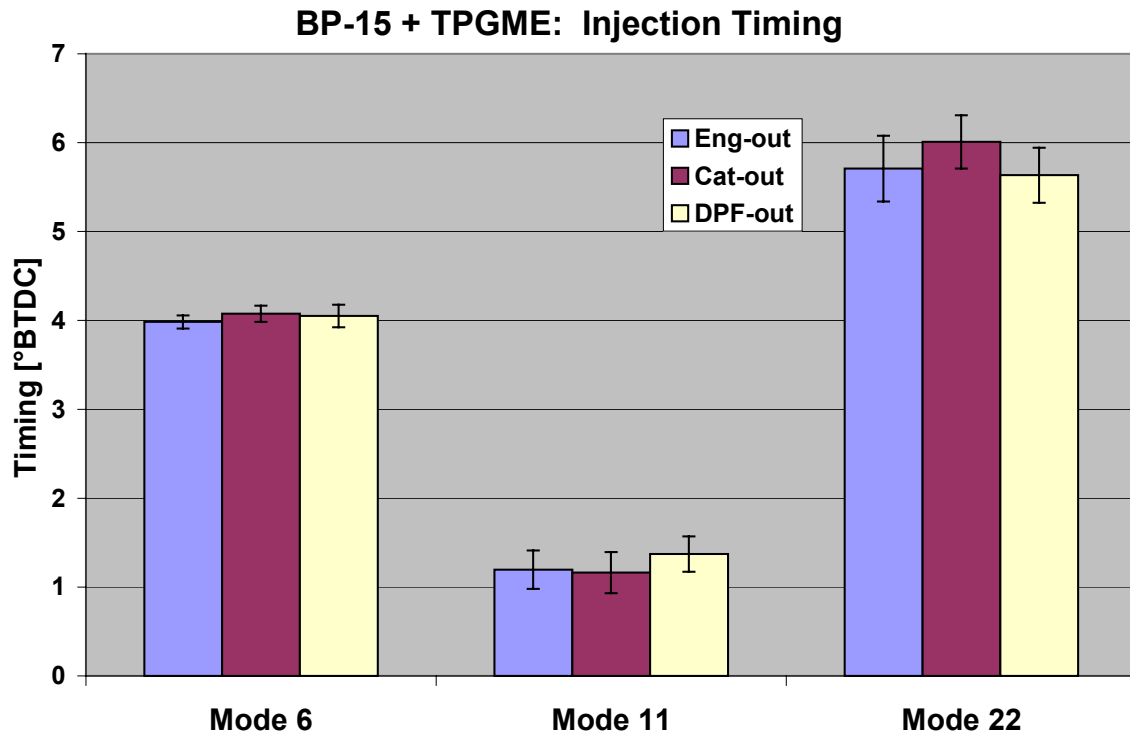


Figure G-1. Injection Timing with TPGME Fuel Additive

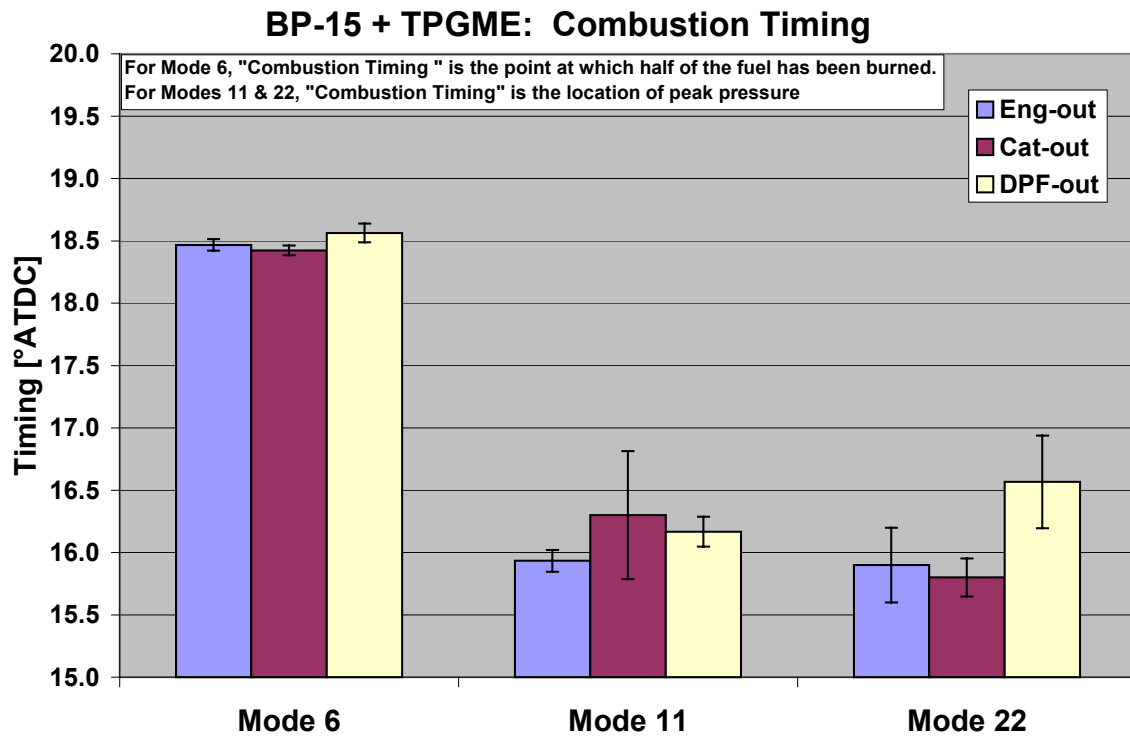


Figure G-2. Combustion Timing with TPGME Fuel Additive

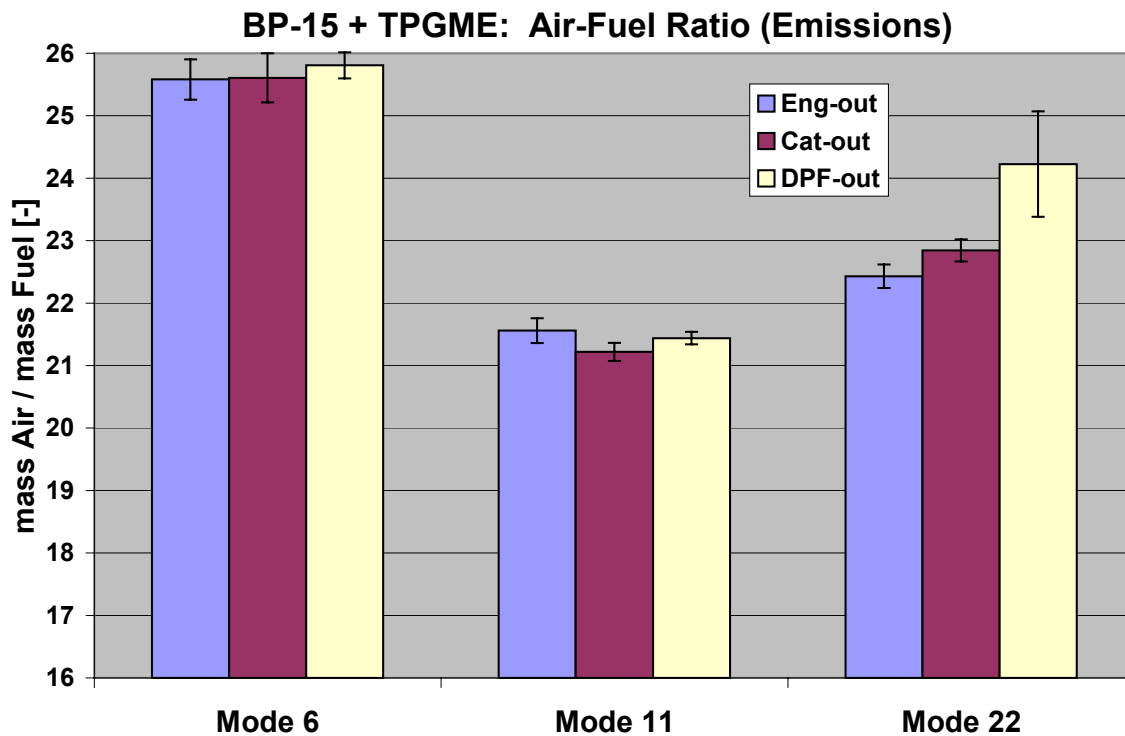


Figure G-3. Emissions Air-Fuel Ratio with TPGME Fuel Additive

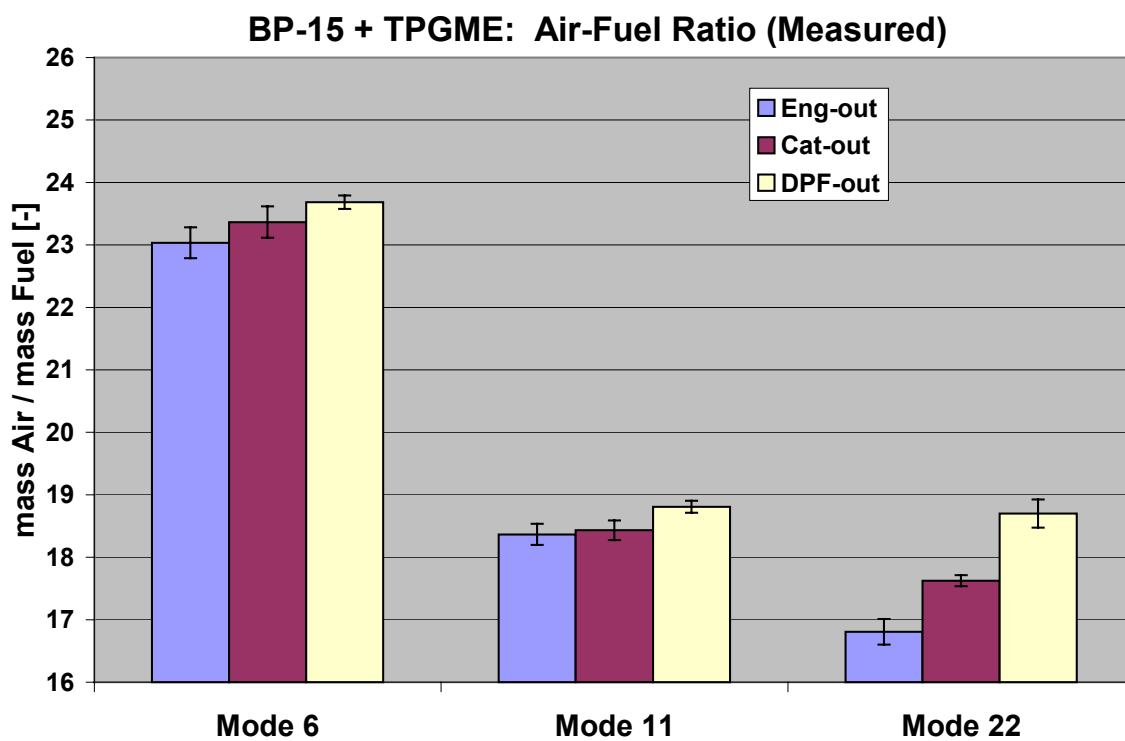


Figure G-4. Measured Air-Fuel Ratio with TPGME Fuel Additive

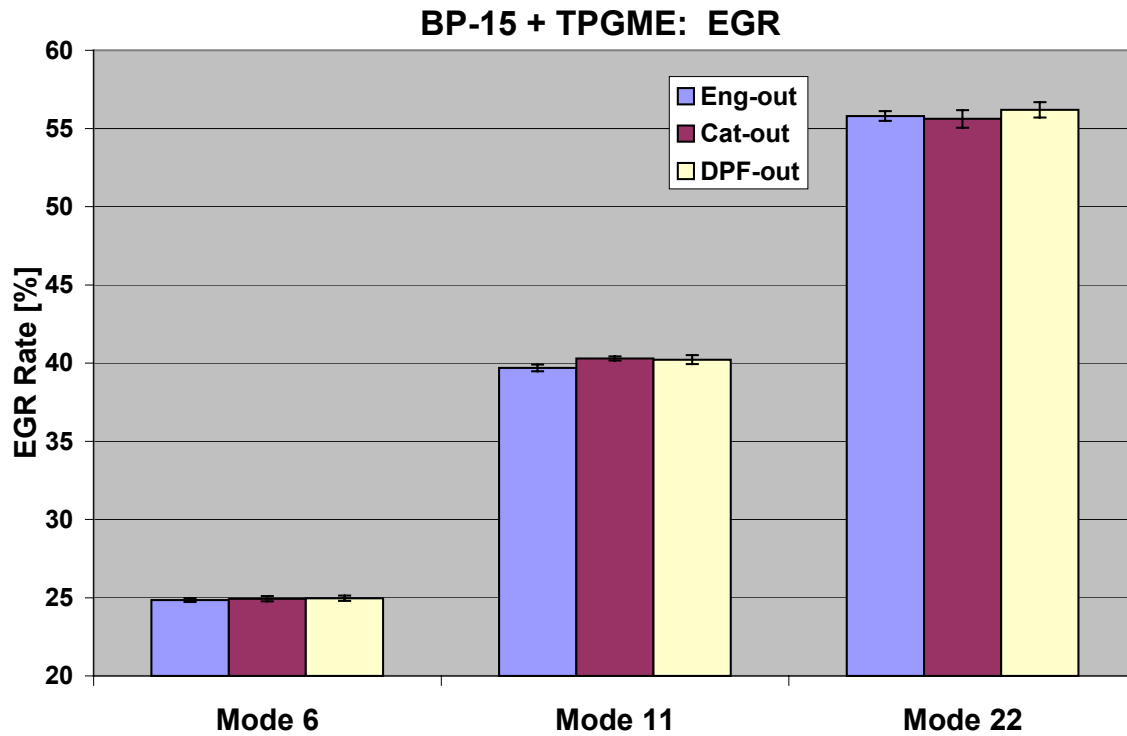


Figure G-5. EGR Rate with TPGME Fuel Additive

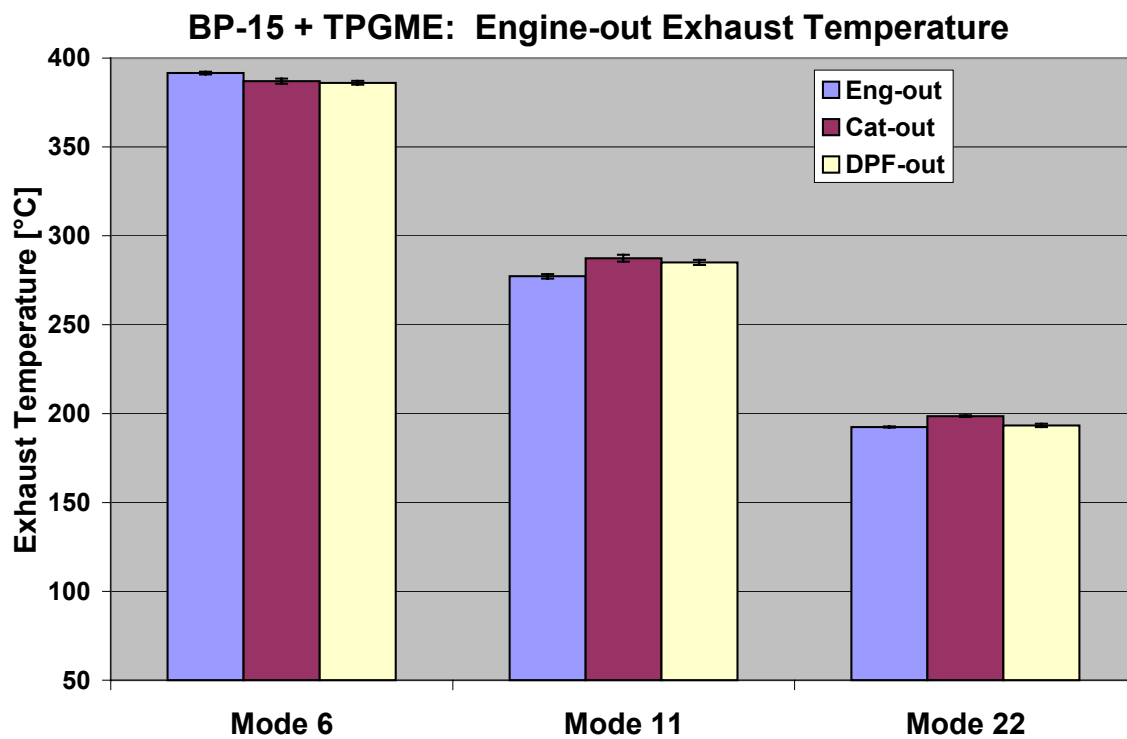


Figure G-6. Engine-Out Exhaust Temperature with TPGME Fuel Additive

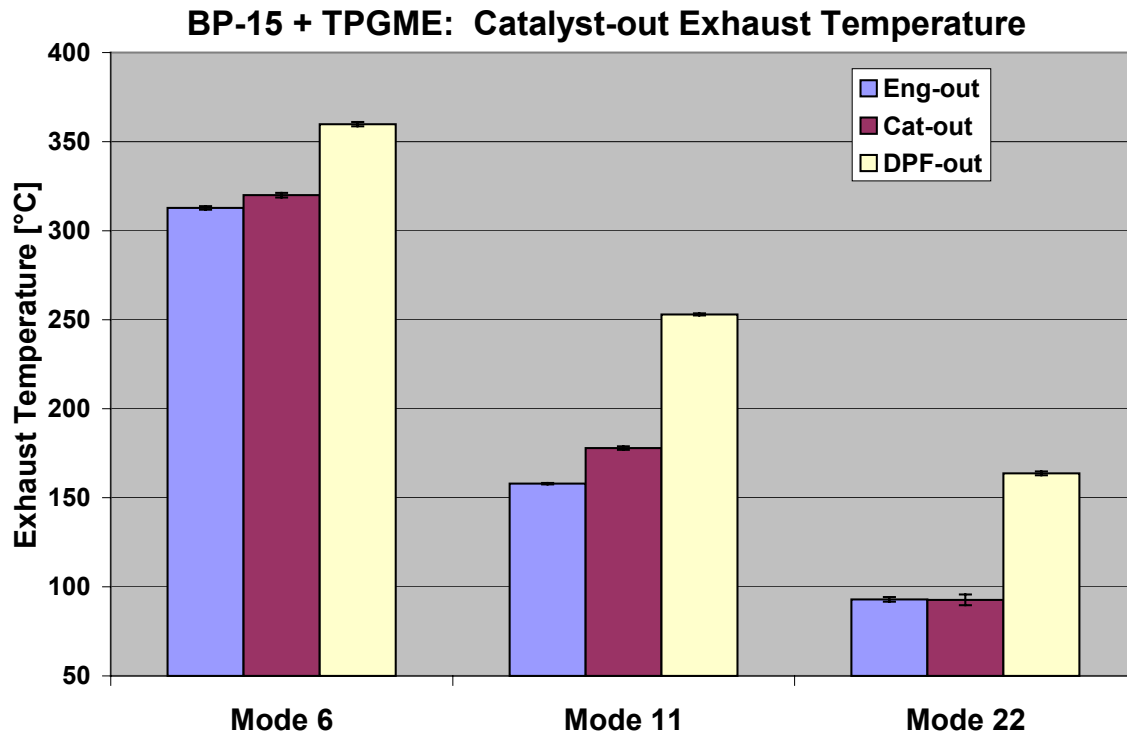


Figure G-7. Catalyst-Out Exhaust Temperature with TPGME Fuel Additive

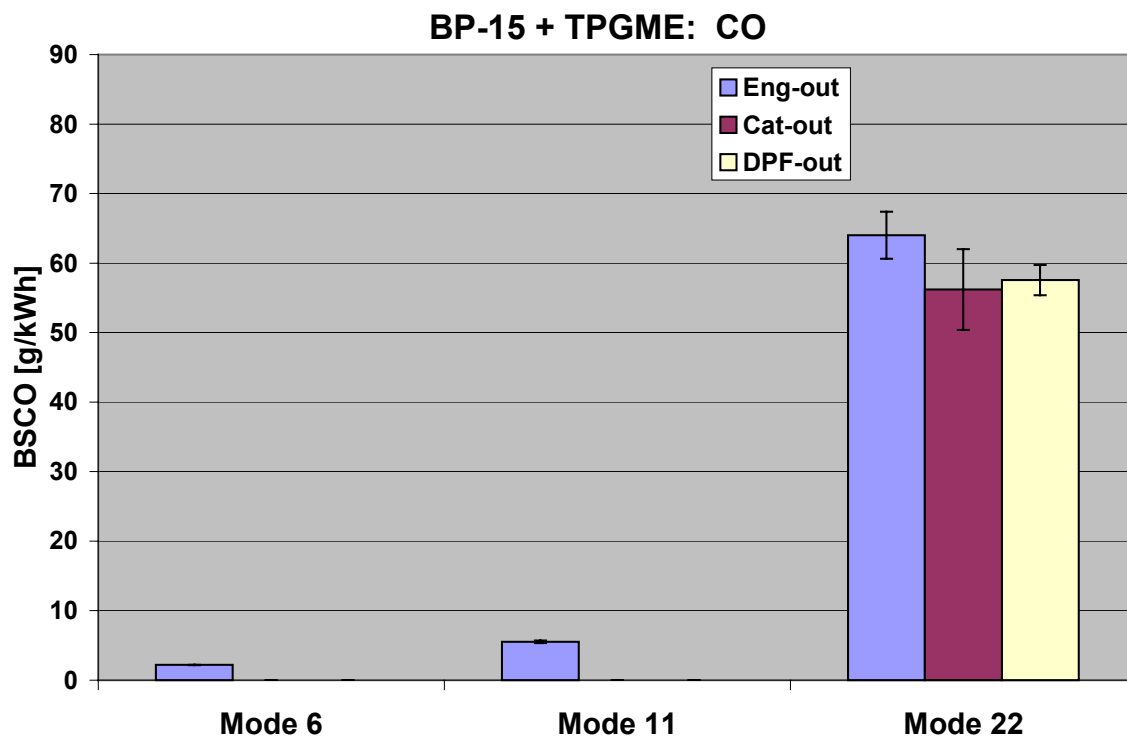


Figure G-8. Carbon Monoxide Emissions with TPGME Fuel Additive

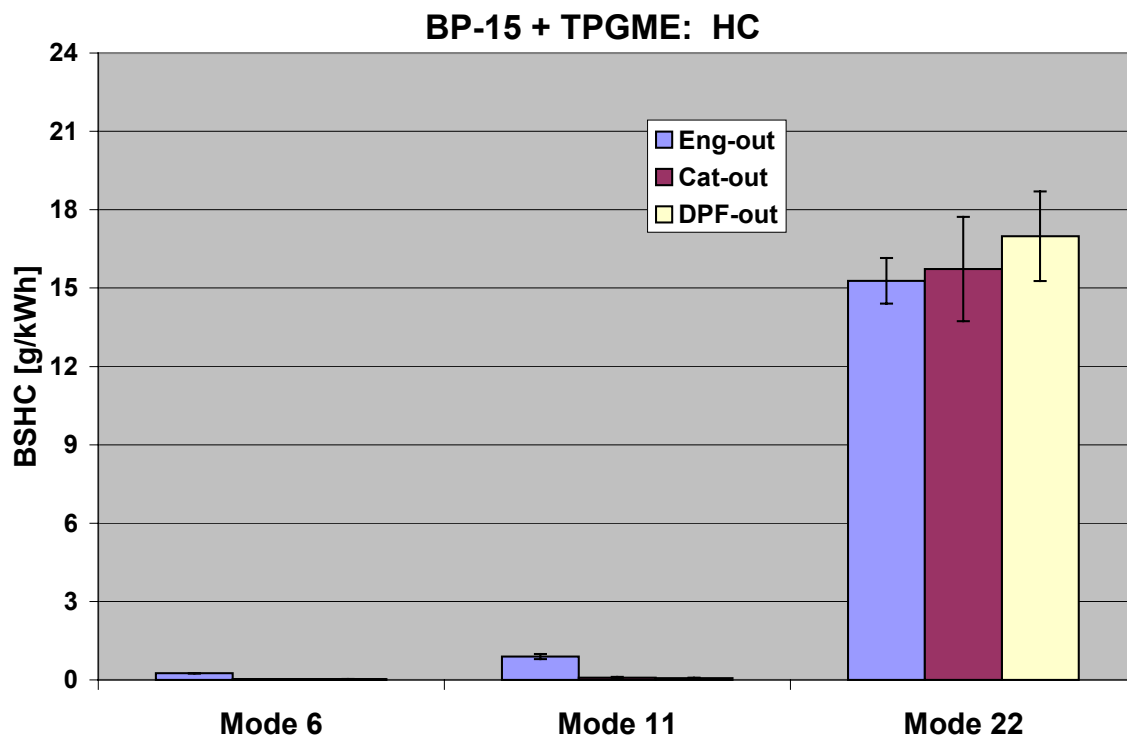


Figure G-9. Hydrocarbon Emissions with TPGME Fuel Additive

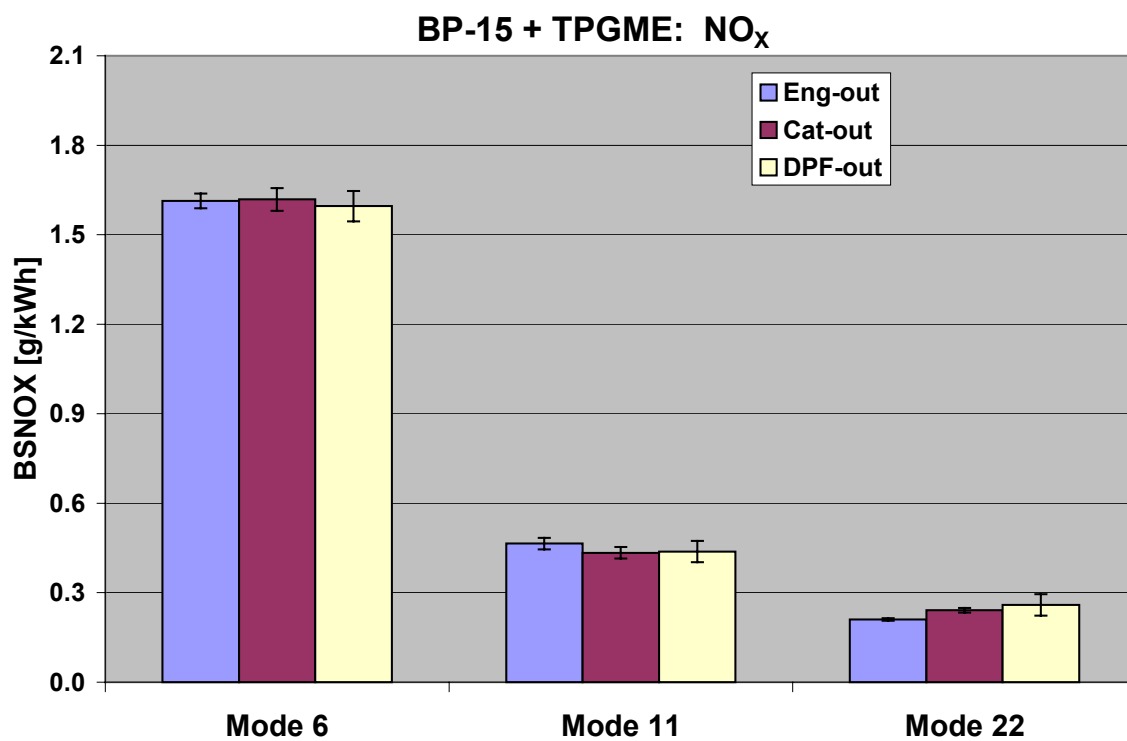


Figure G-10. Nitrogen Oxides Emissions with TPGME Fuel Additive

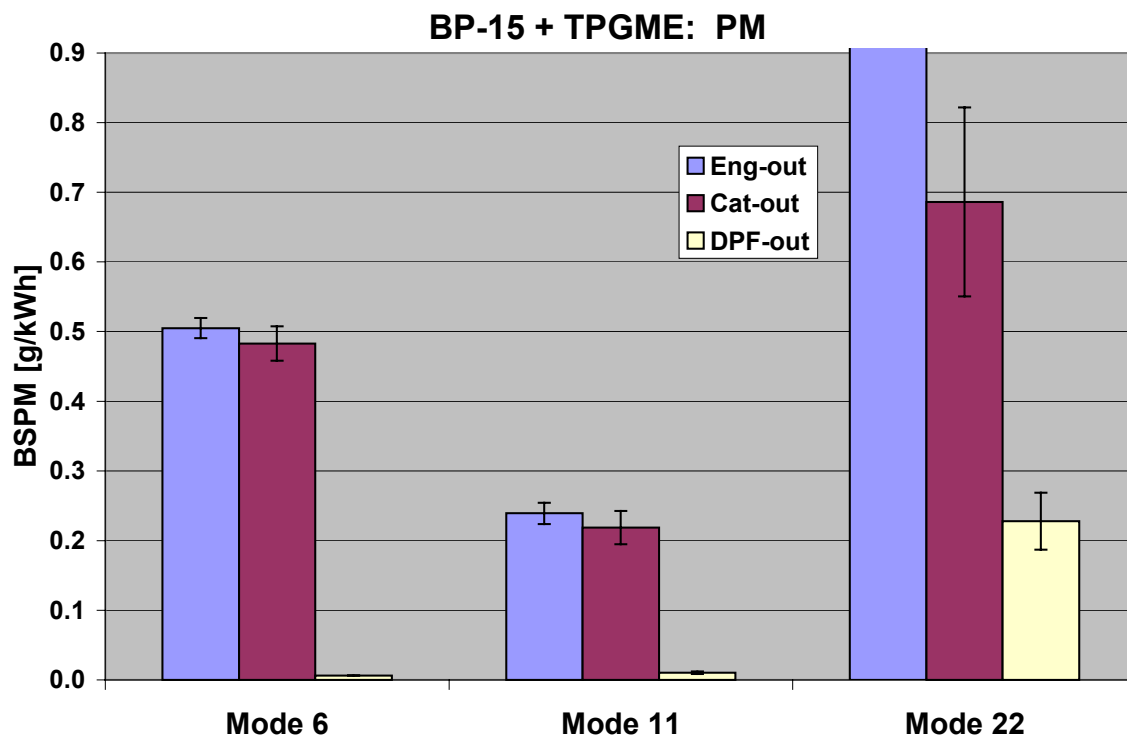


Figure G-11. Particulate Matter Emissions with TPGME Fuel Additive

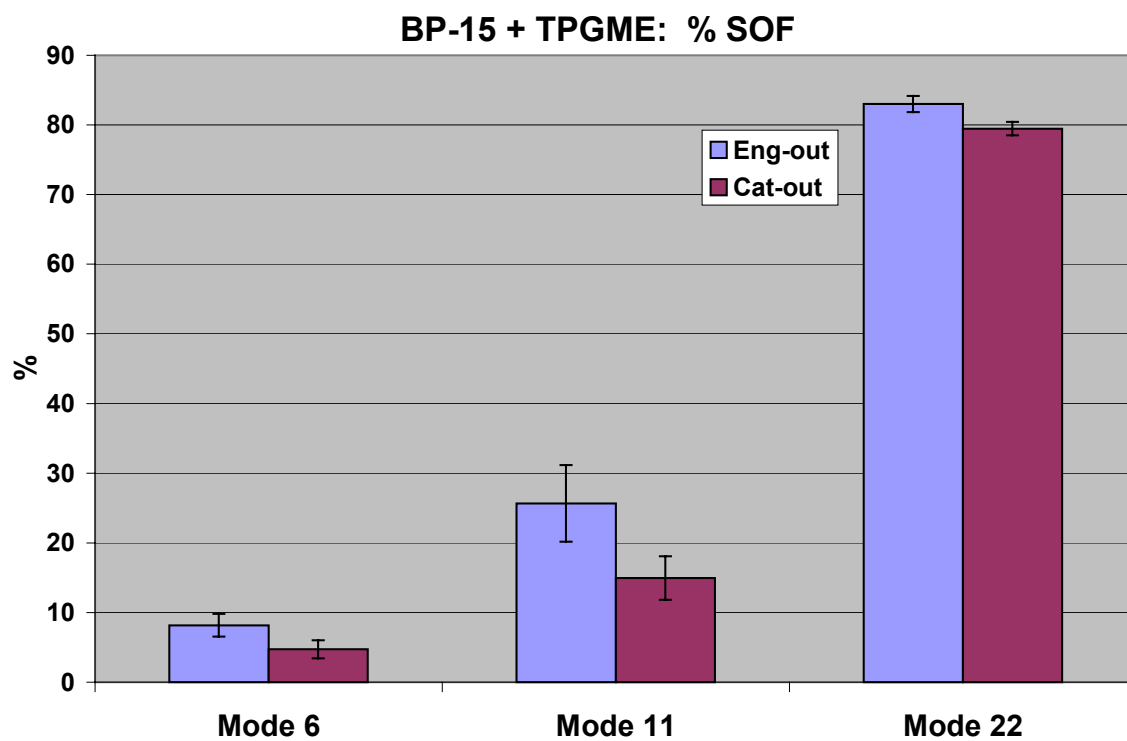


Figure G-12. Percent Soluble Organic Fraction with TPGME Fuel Additive

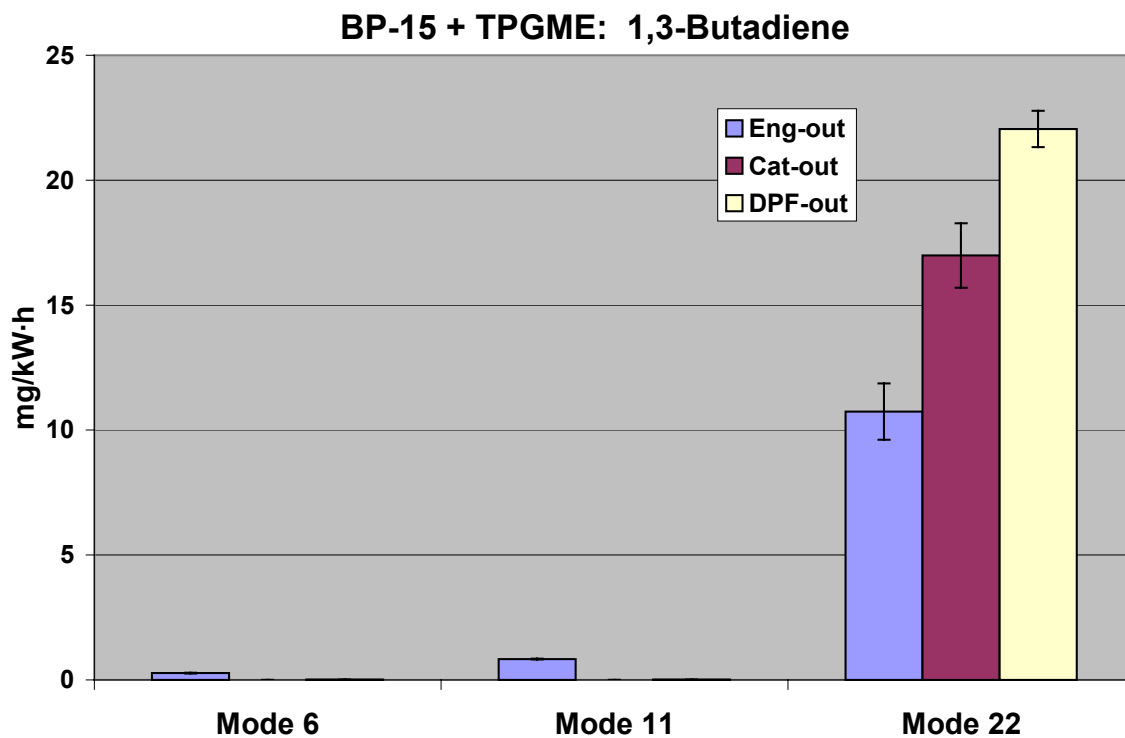


Figure G-13. 1,3-Butadiene Emissions with TPGME Fuel Additive

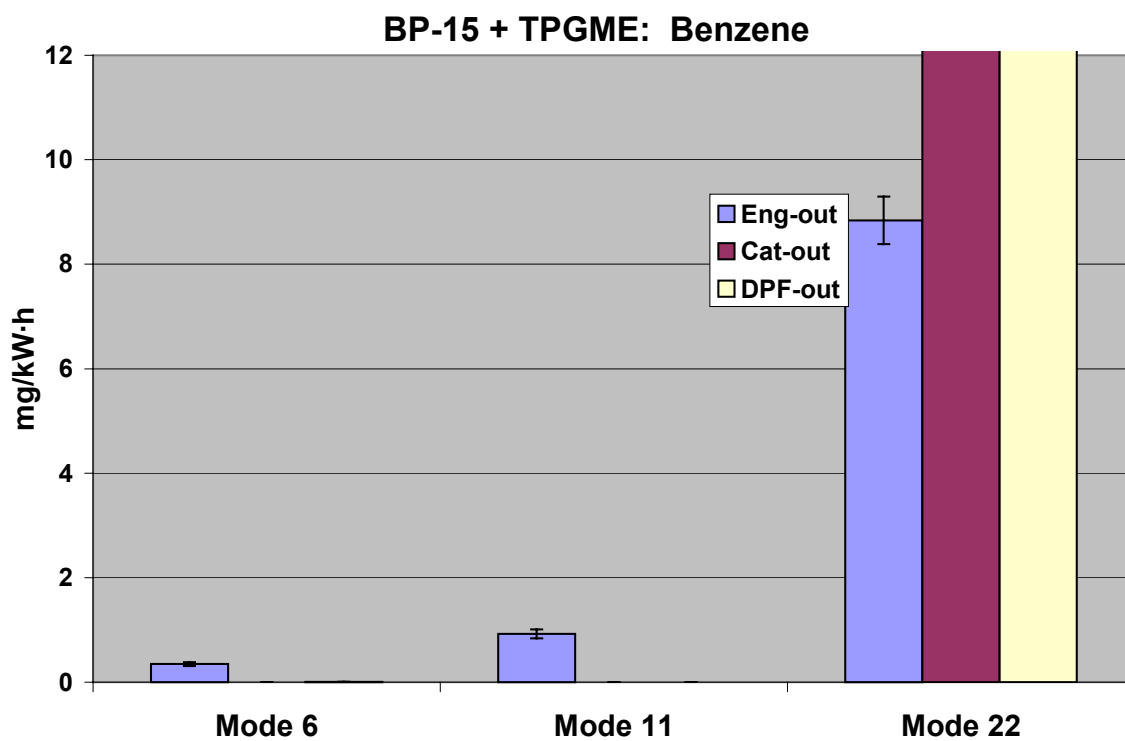


Figure G-14. Benzene Emissions with TPGME Fuel Additive

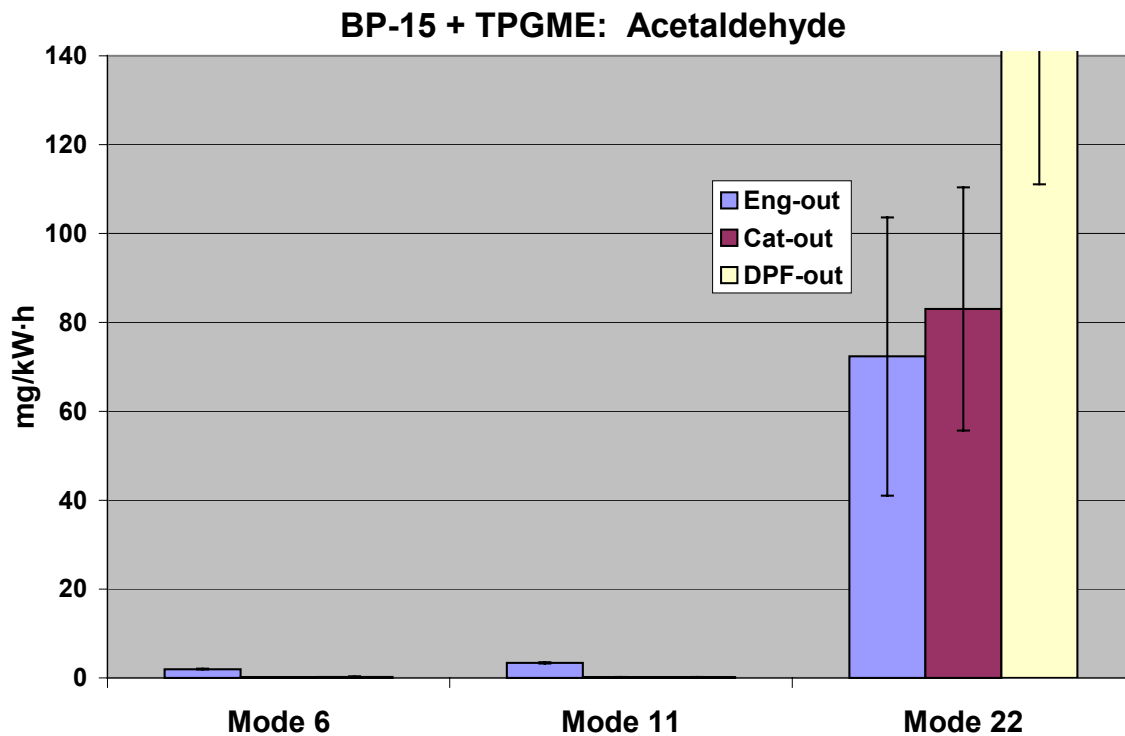


Figure G-15. Acetaldehyde Emissions with TPGME Fuel Additive

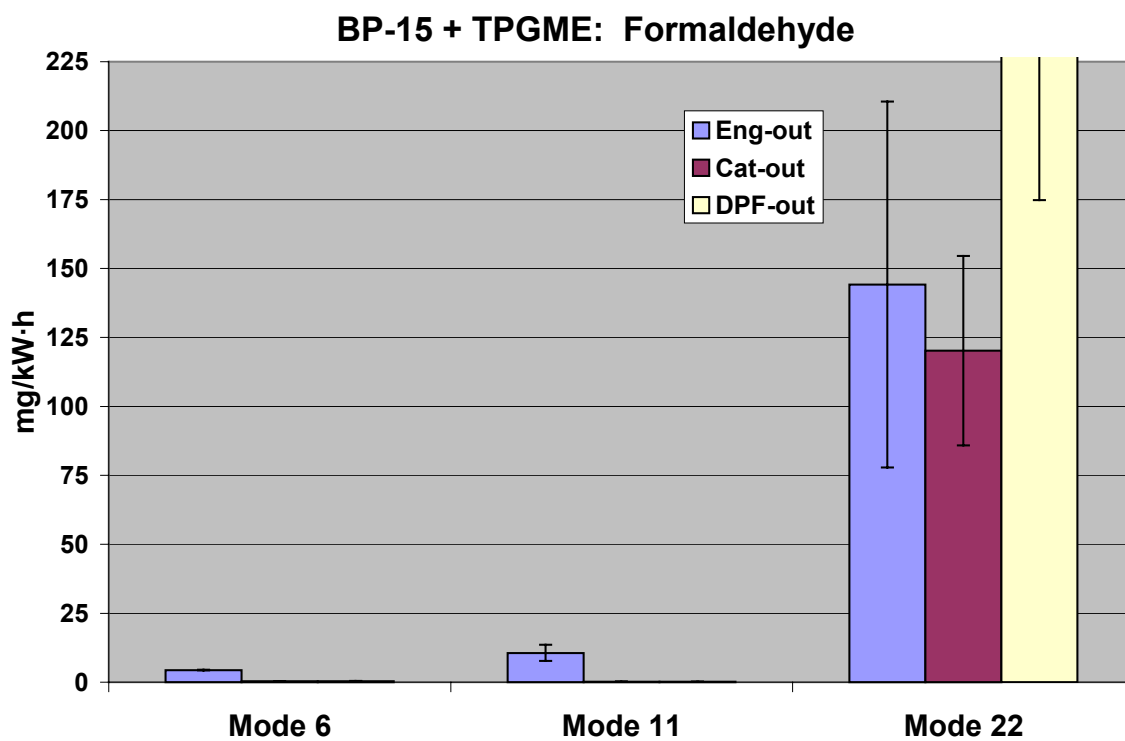


Figure G-16. Formaldehyde Emissions with TPGME Fuel Additive



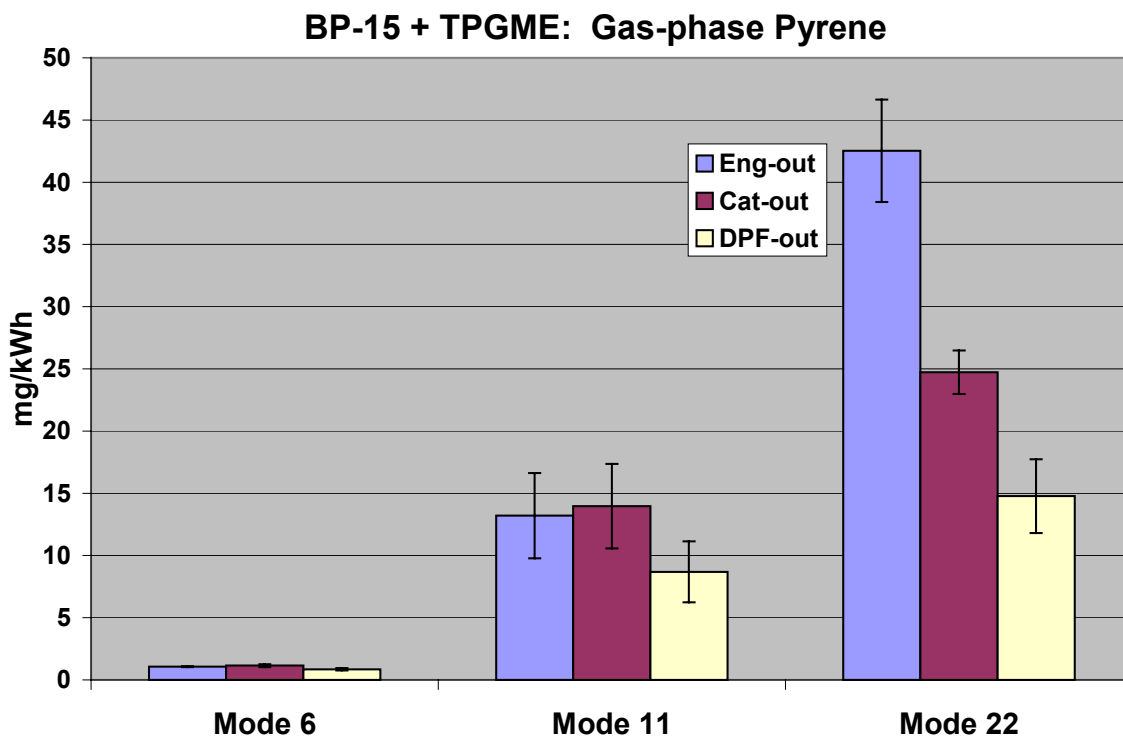


Figure G-17. Gas-Phase Pyrene Emissions with TPGME Fuel Additive

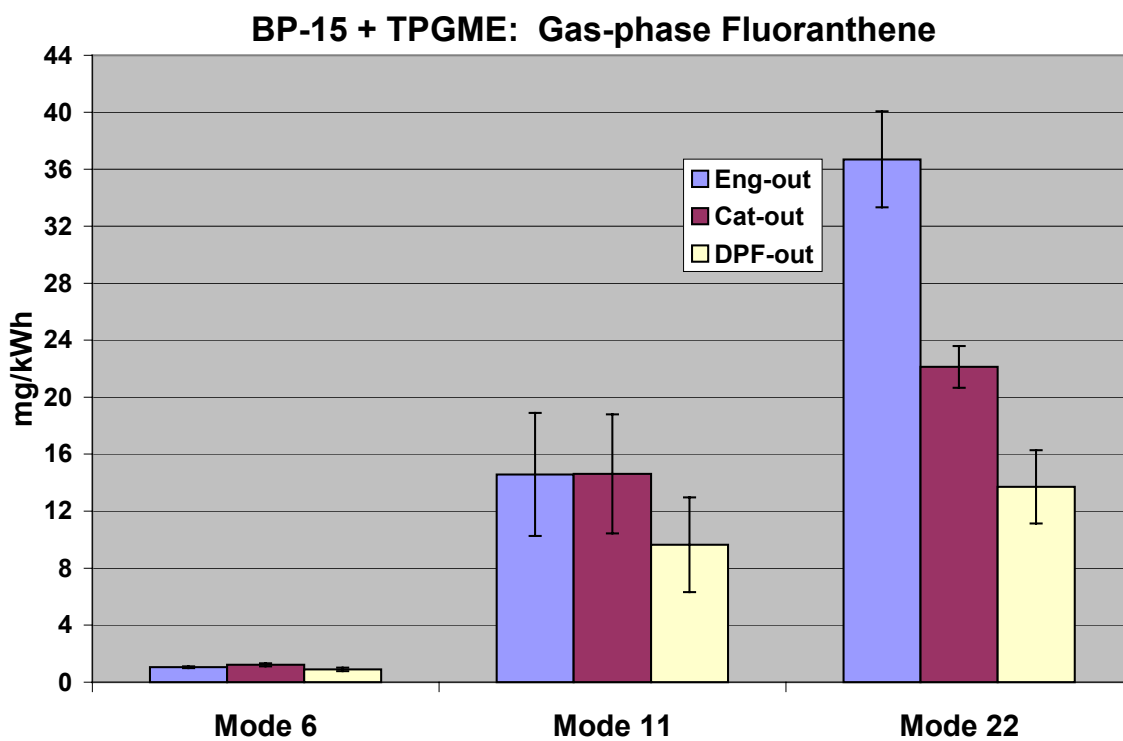


Figure G-18. Gas-Phase Fluoranthene Emissions with TPGME Fuel Additive

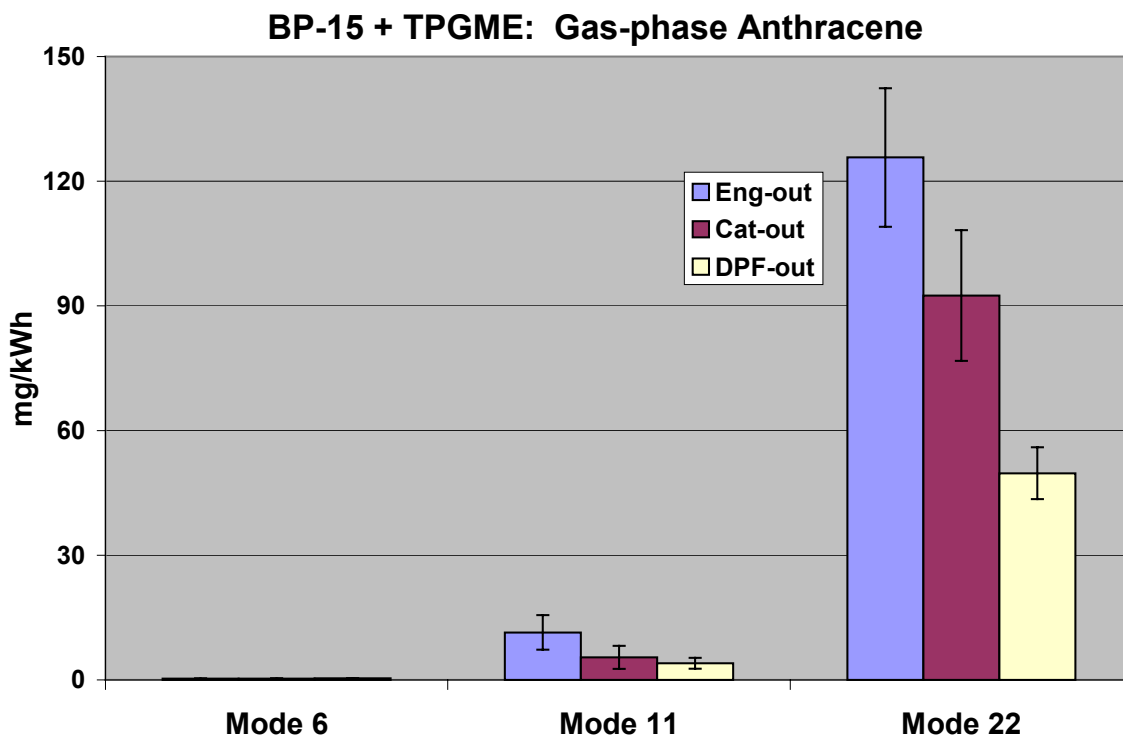


Figure G-19. Gas-Phase Anthracene Emissions with TPGME Fuel Additive

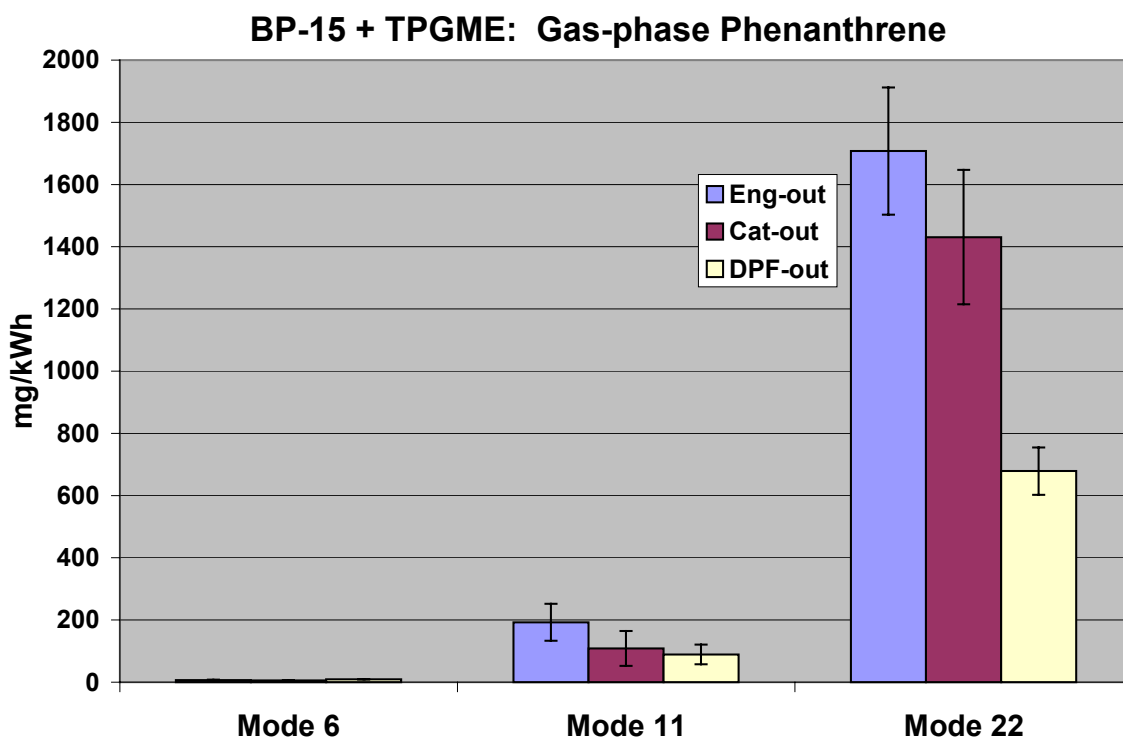


Figure G-20. Gas-Phase Phenanthrene Emissions with TPGME Fuel Additive

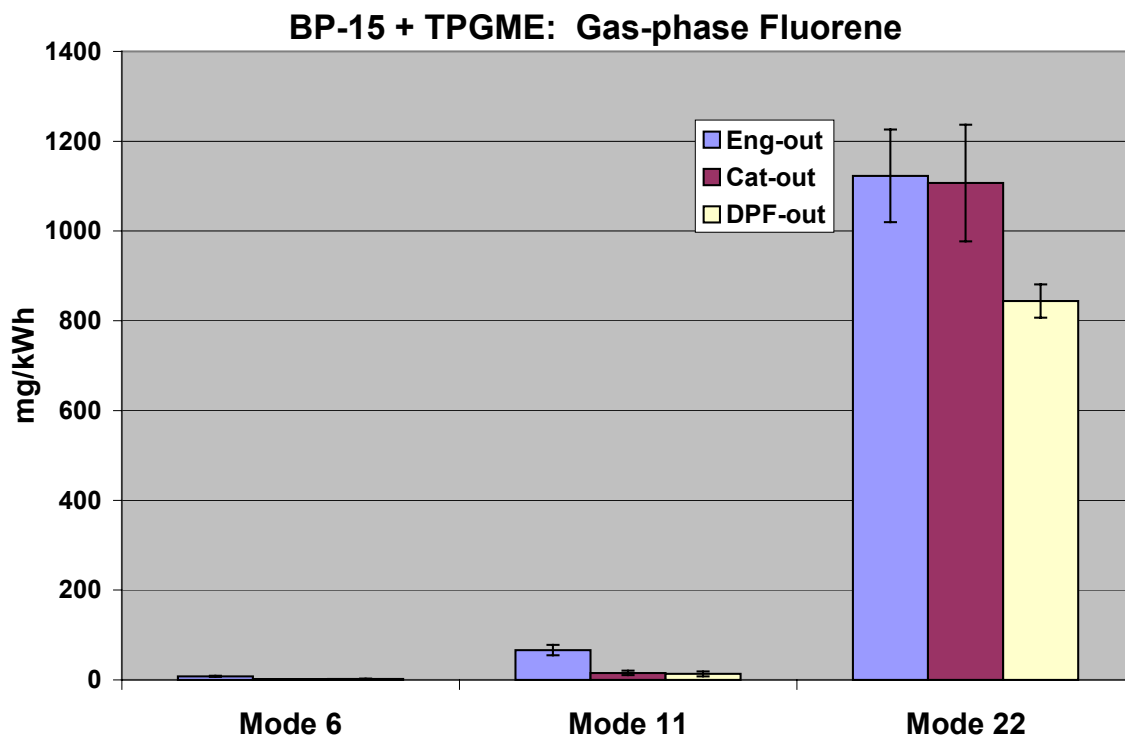


Figure G-21. Gas-Phase Fluorene Emissions with TPGME Fuel Additive

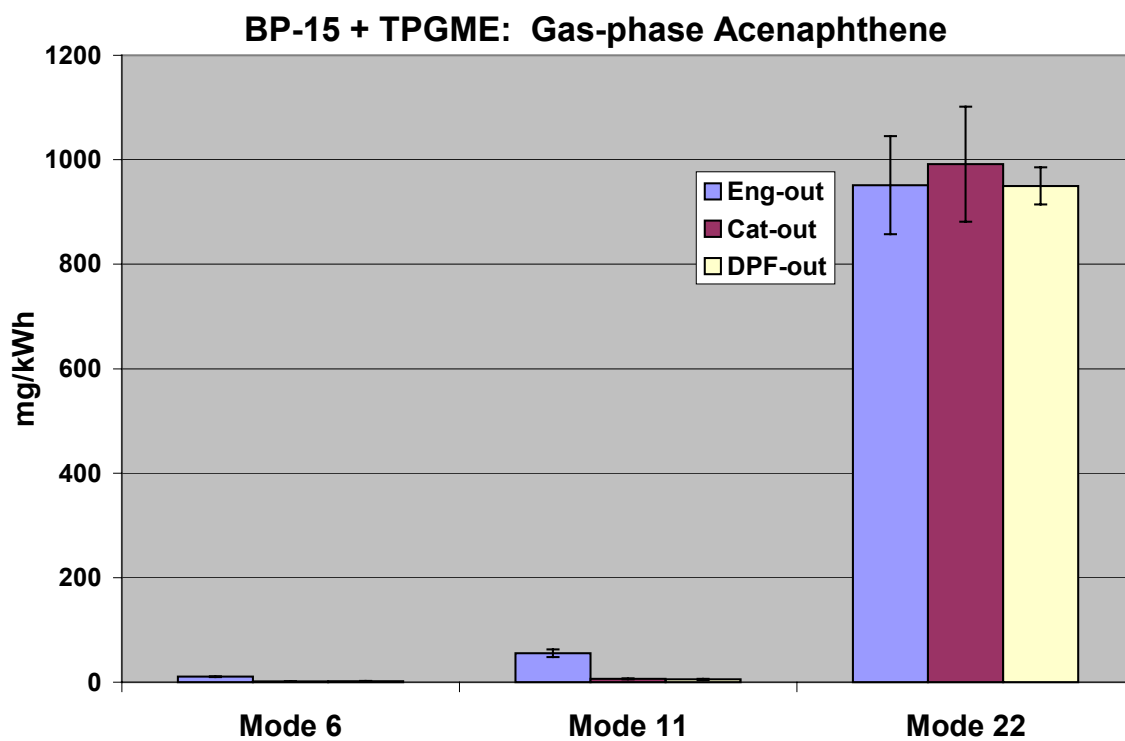


Figure G-22. Gas-Phase Acenaphthene Emissions with TPGME Fuel Additive

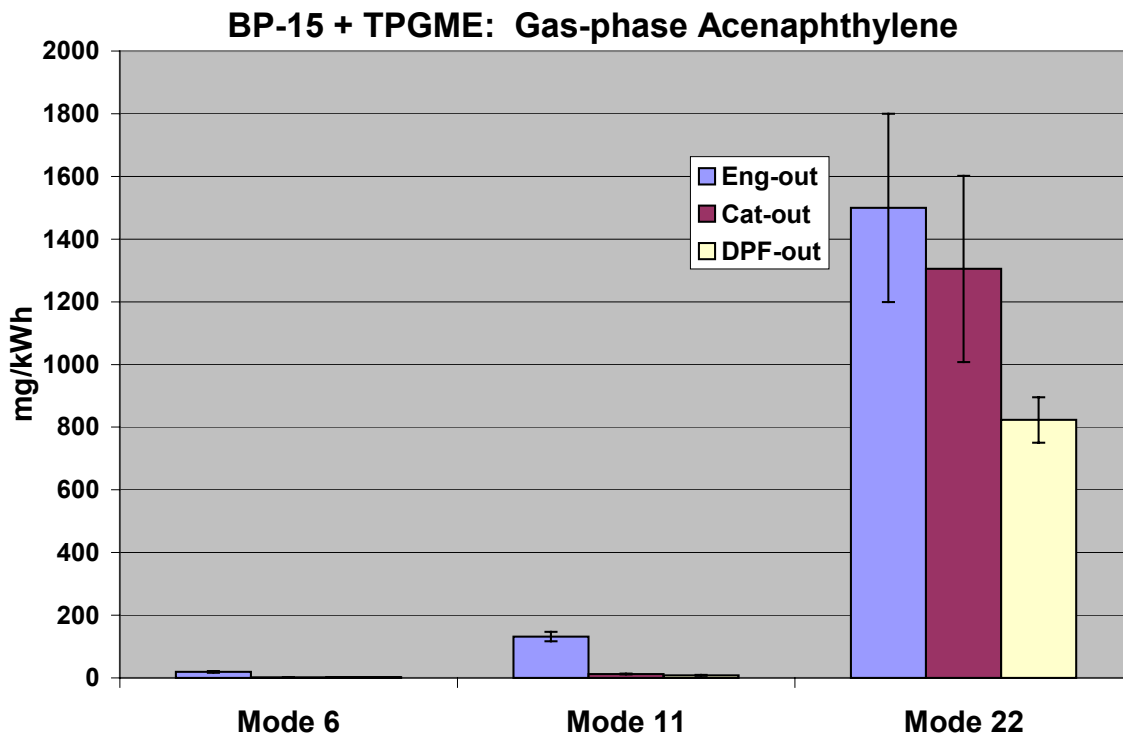


Figure G-23. Gas-Phase Acenaphthylene Emissions with TPGME Fuel Additive

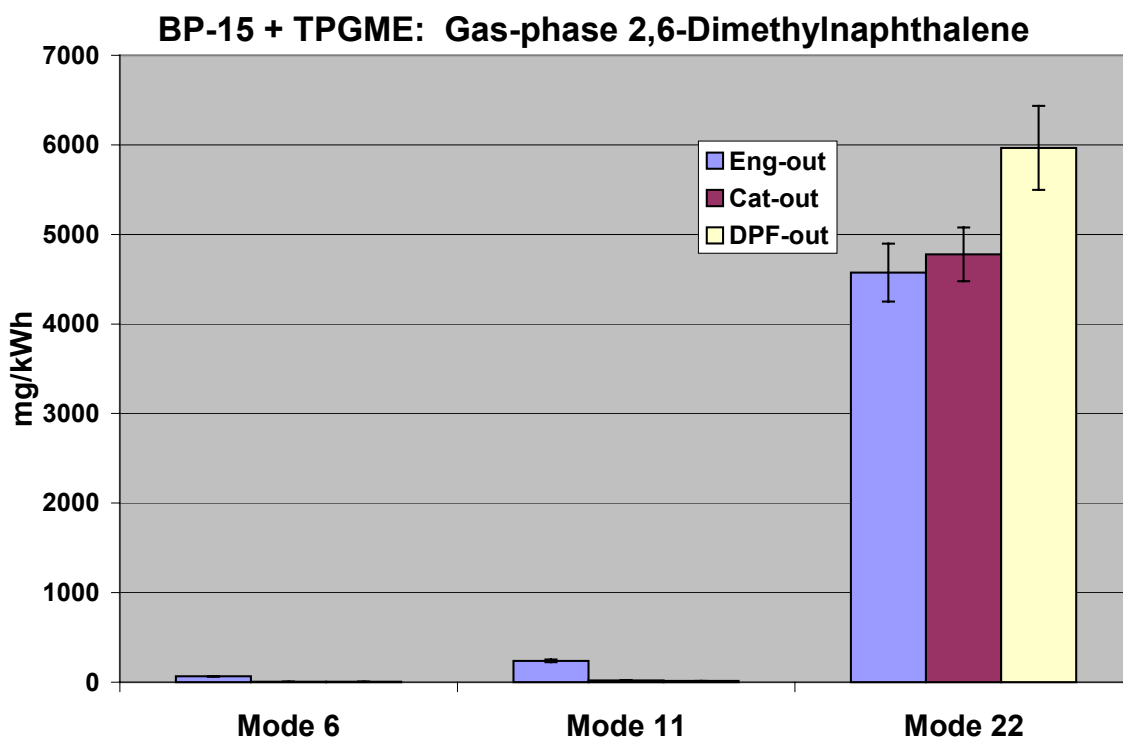


Figure G-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions with TPGME Fuel Additive

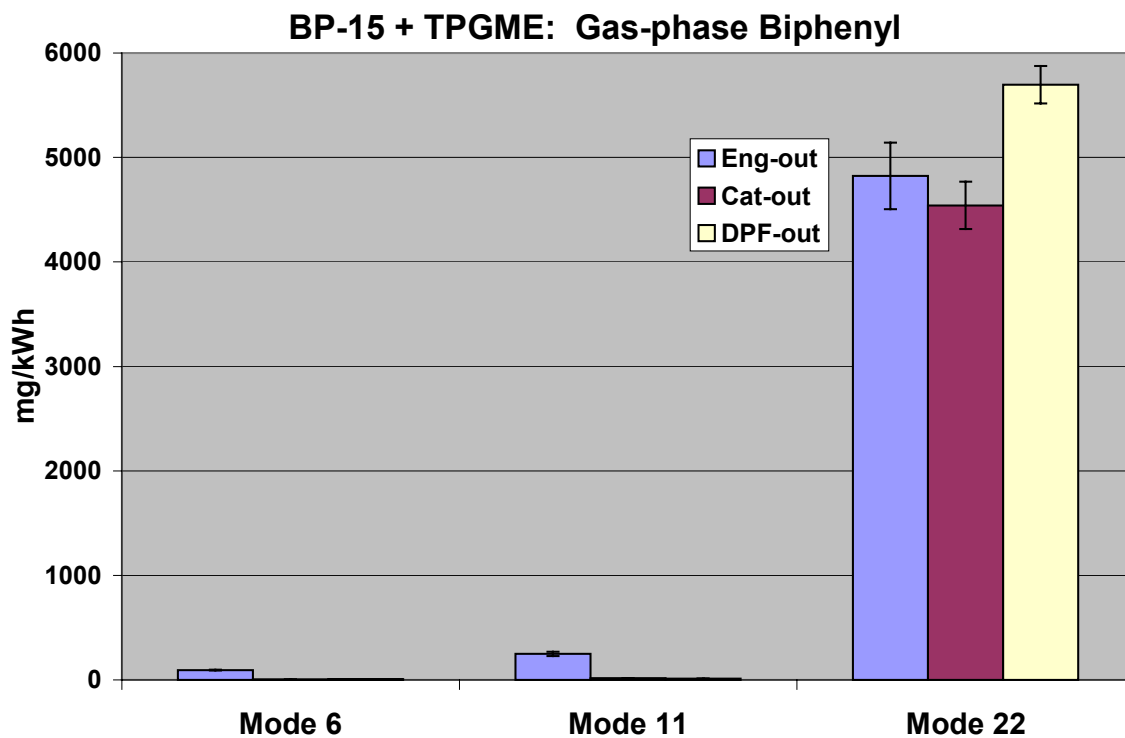


Figure G-25. Gas-Phase Biphenyl Emissions with TPGME Fuel Additive

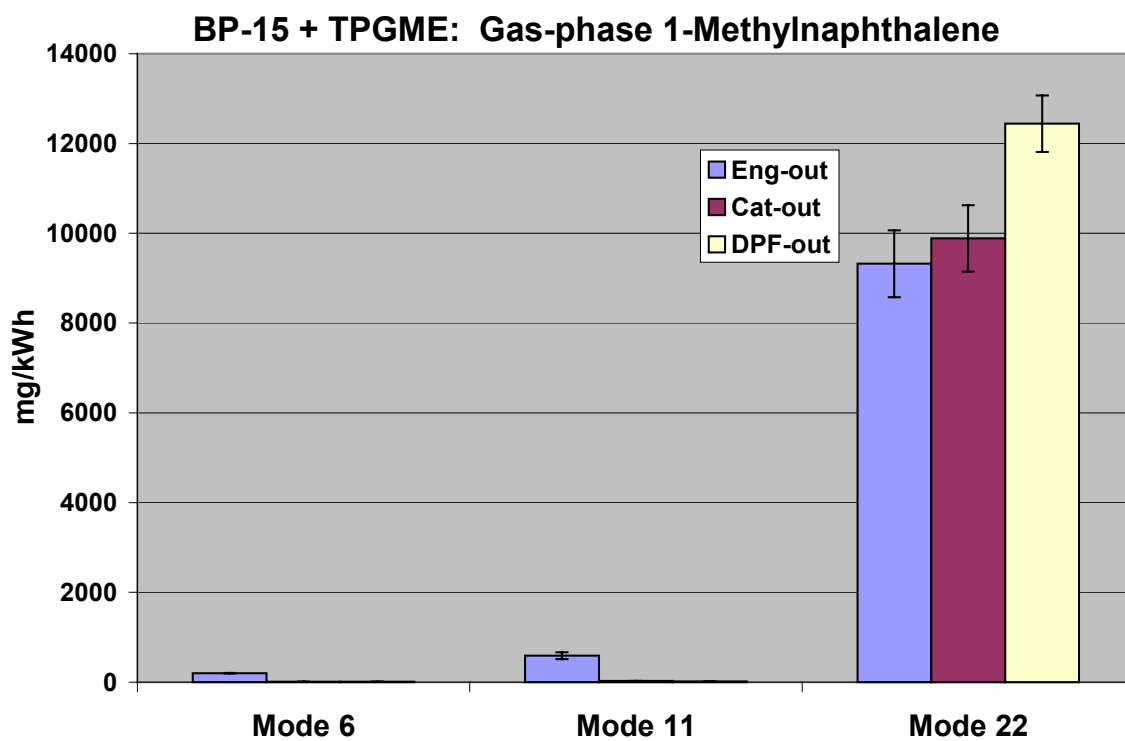


Figure G-26. Gas-Phase 1-Methylnaphthalene Emissions with TPGME Fuel Additive

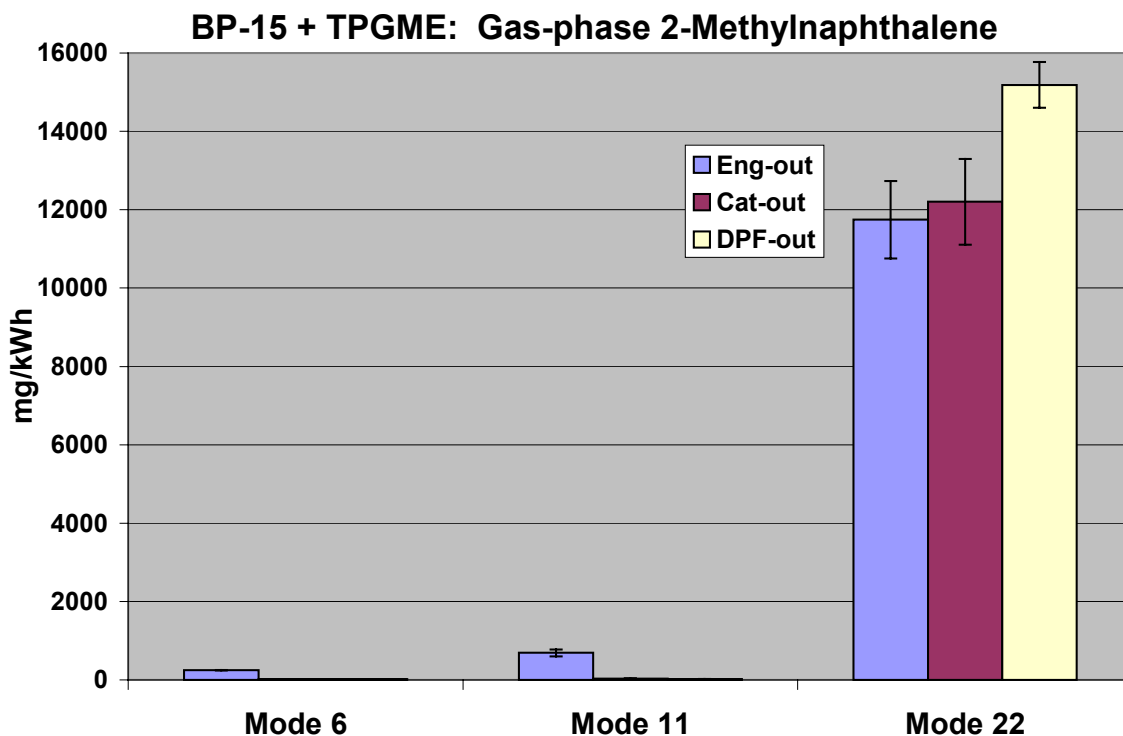


Figure G-27. Gas-Phase 2-Methylnaphthalene Emissions with TPGME Fuel Additive

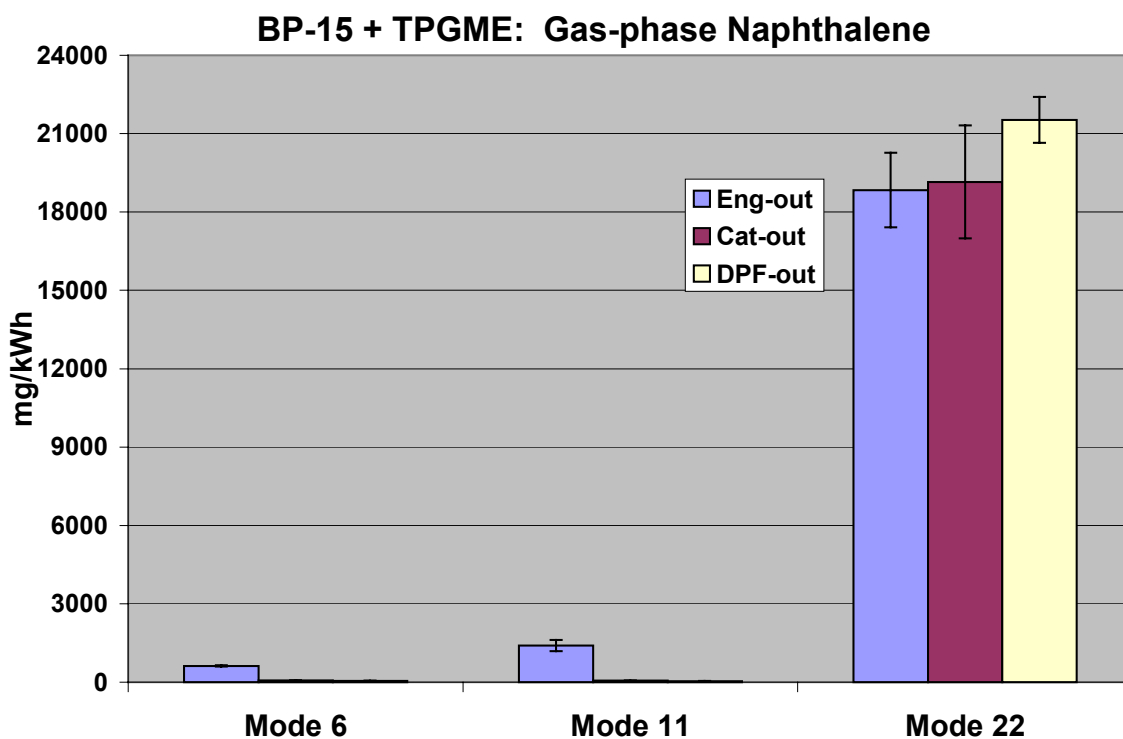


Figure G-28. Gas-Phase Naphthalene Emissions with TPGME Fuel Additive

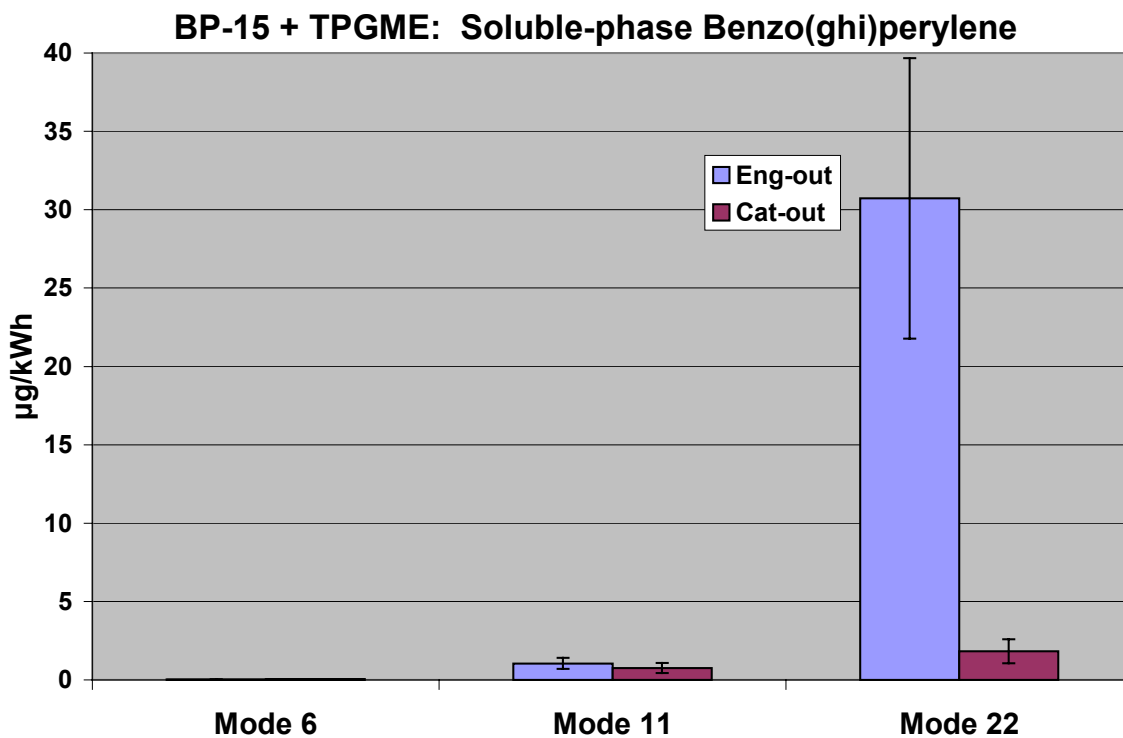


Figure G-29. Soluble-Phase Benzo(ghi)perylene Emissions with TPGME Fuel Additive

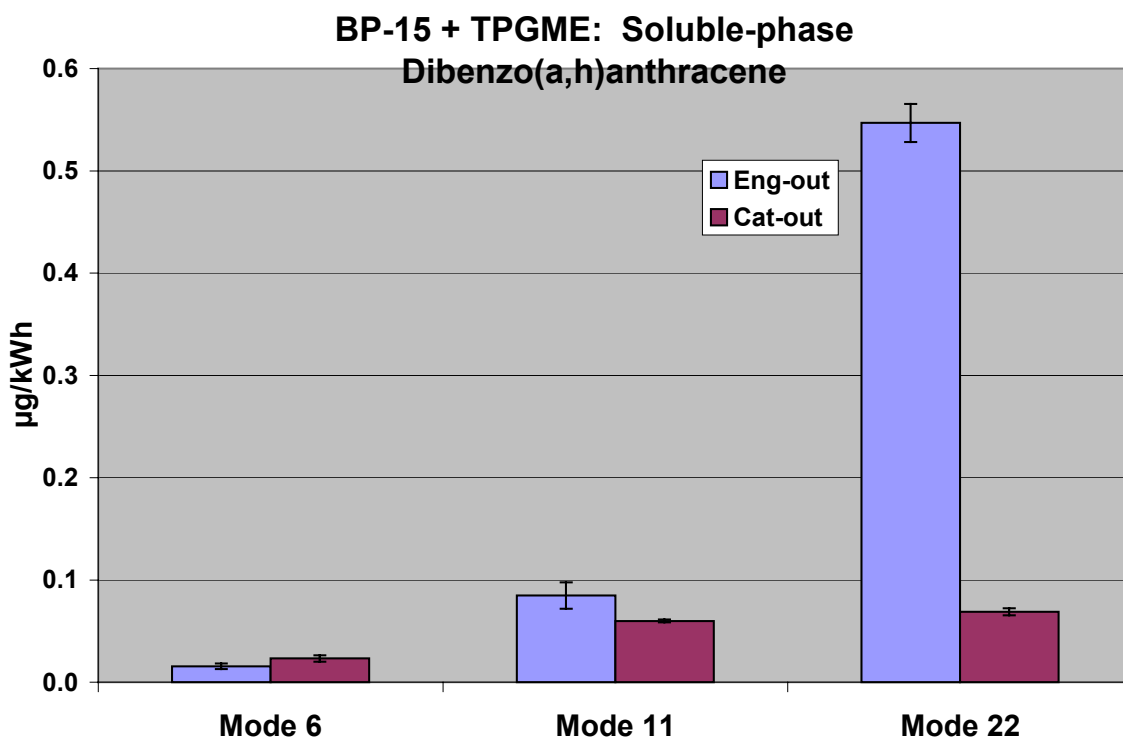


Figure G-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions with TPGME Fuel Additive

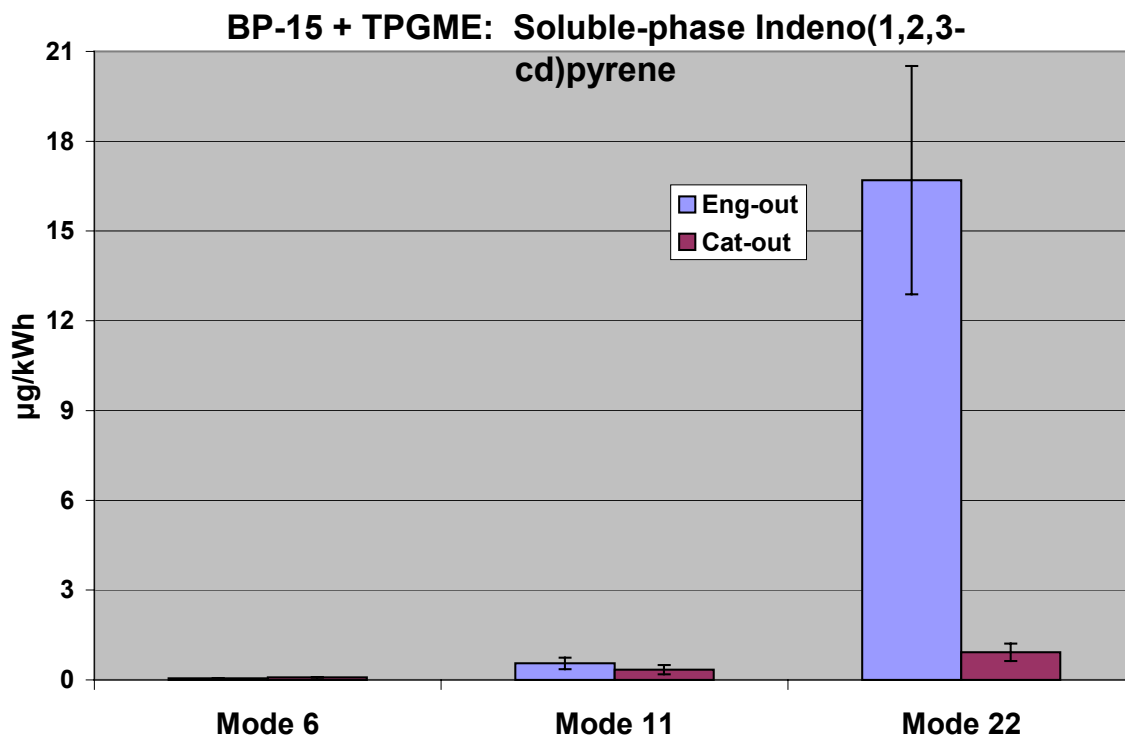


Figure G-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions with TPGME Fuel Additive

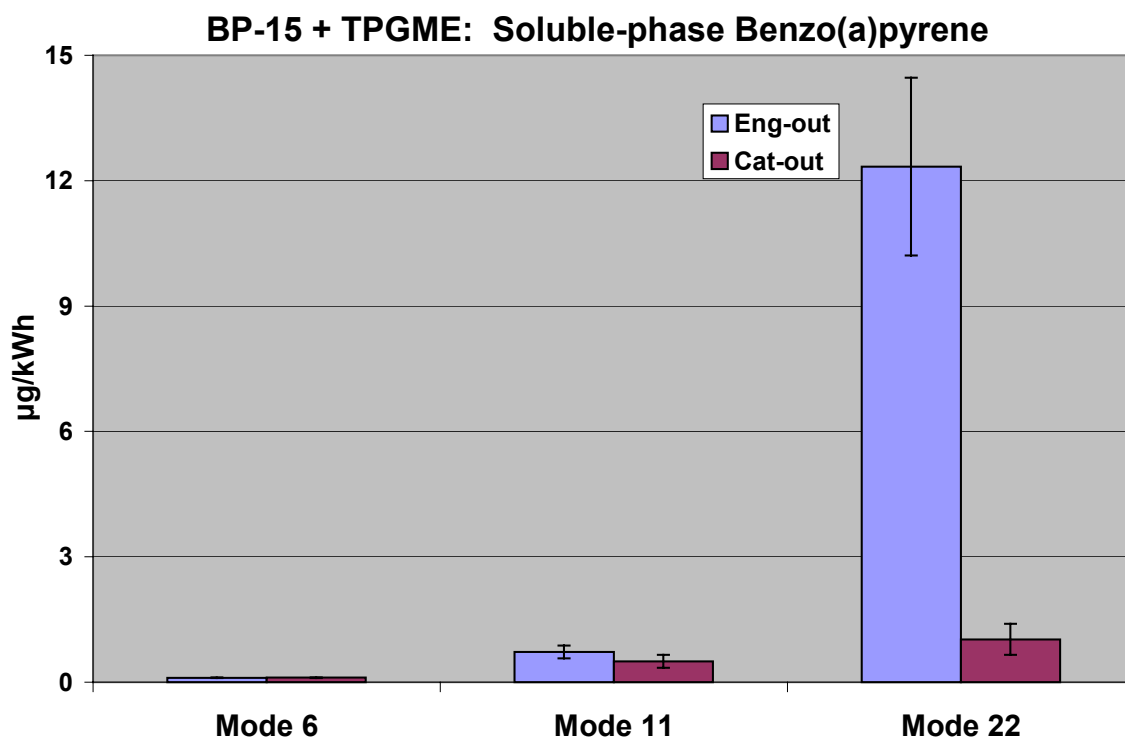


Figure G-32. Soluble-Phase Benzo(a)pyrene Emissions with TPGME Fuel Additive



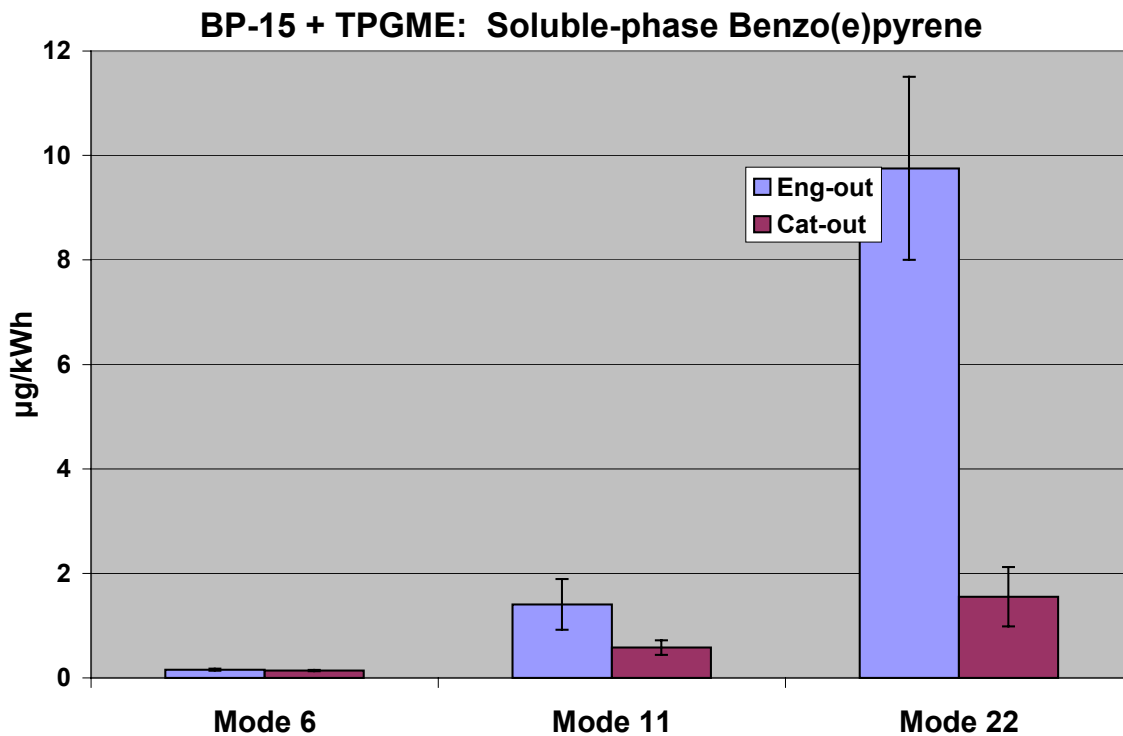


Figure G-33. Soluble-Phase Benzo(e)pyrene Emissions with TPGME Fuel Additive

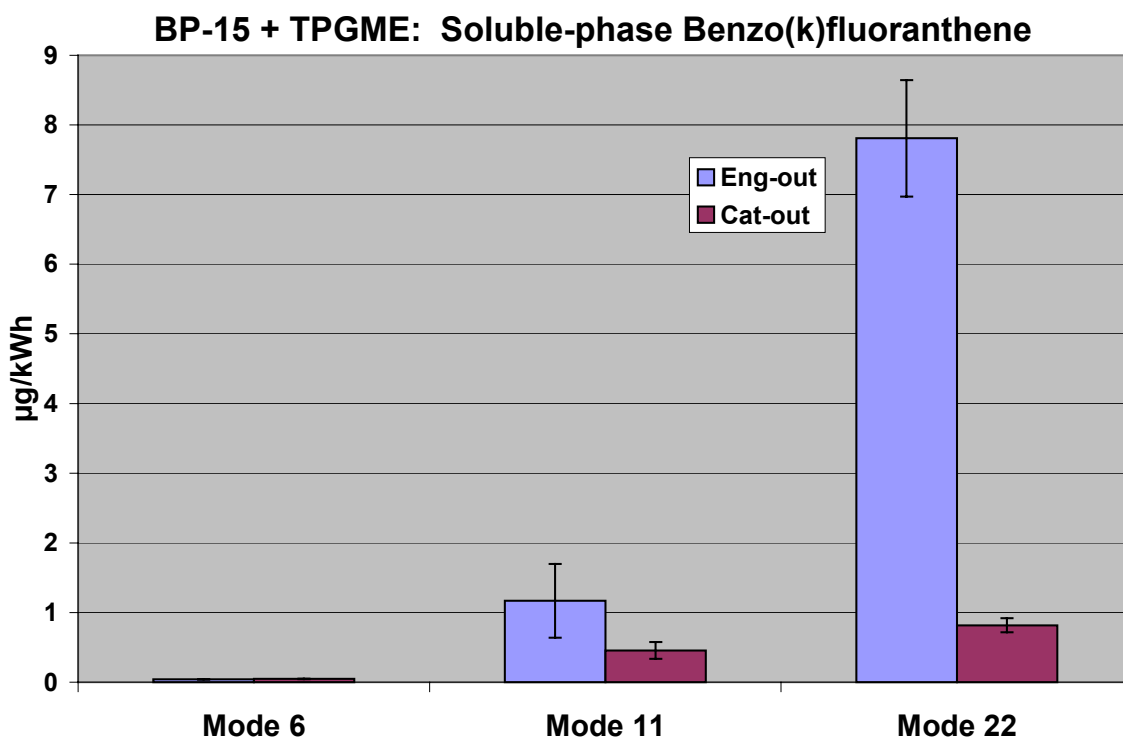


Figure G-34. Soluble-Phase Benzo(k)fluoranthene Emissions with TPGME Fuel Additive

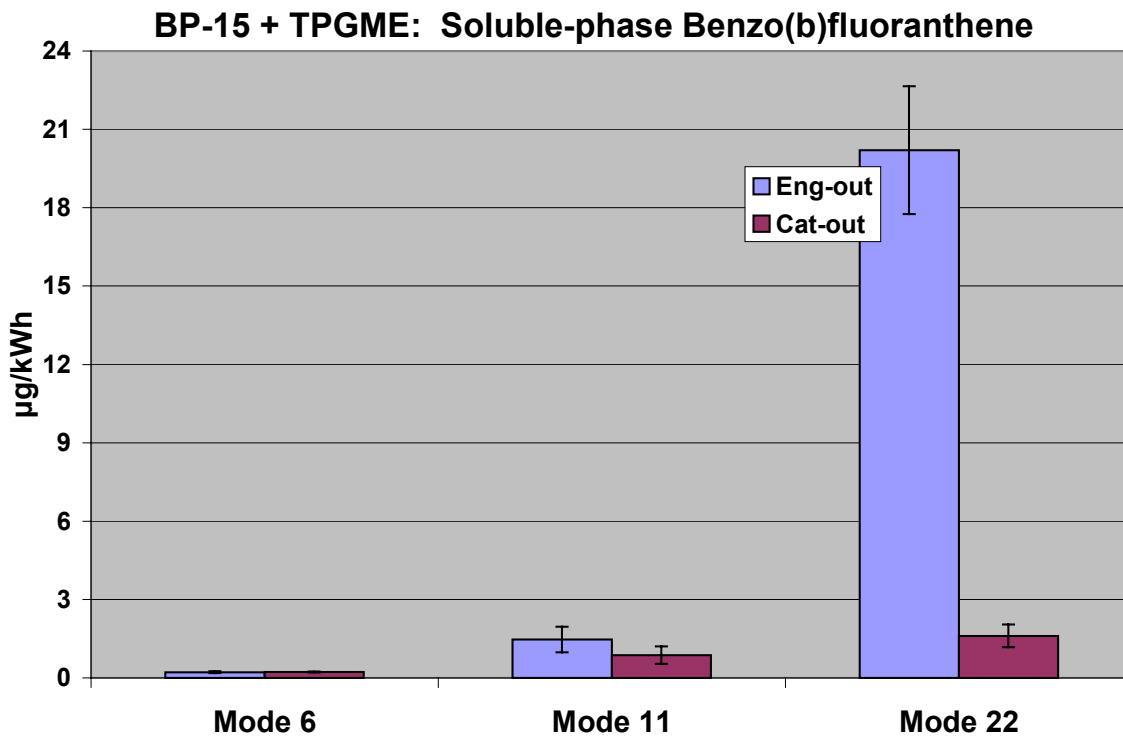


Figure G-35. Soluble-Phase Benzo(b)fluoranthene Emissions with TPGME Fuel Additive

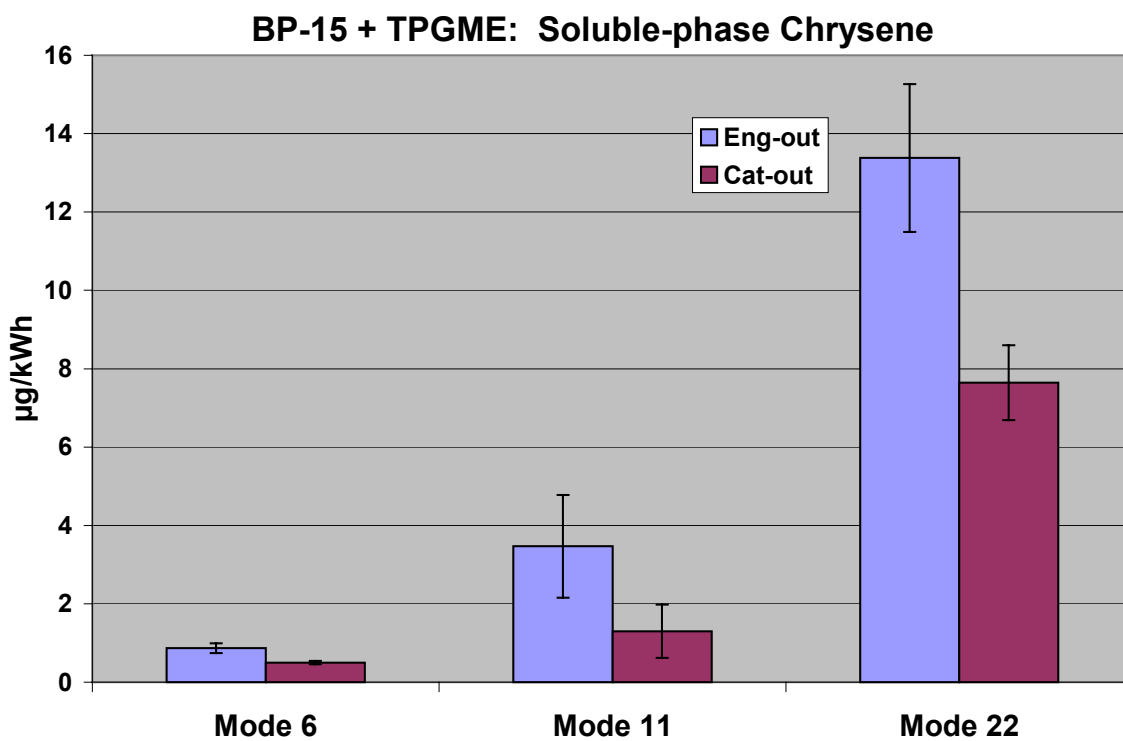


Figure G-36. Soluble-Phase Chrysene Emissions with TPGME Fuel Additive

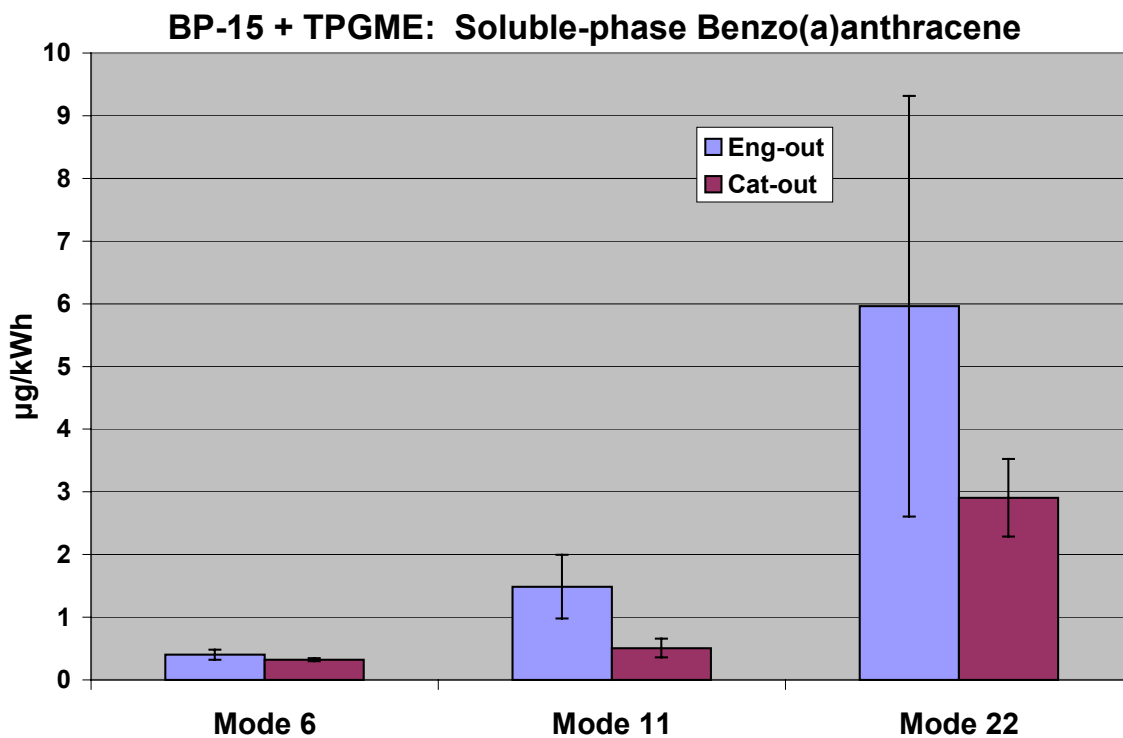


Figure G-37. Soluble-Phase Benzo(a)anthracene Emissions with TPGME Fuel Additive

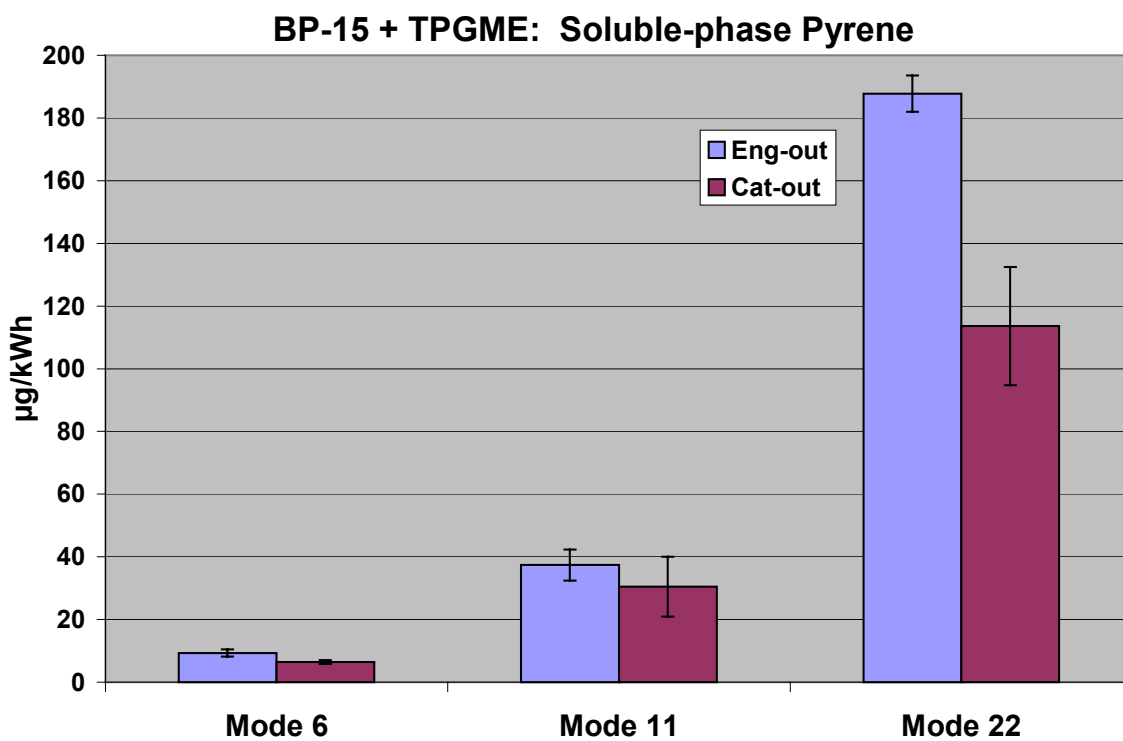


Figure G-38. Soluble-Phase Pyrene Emissions with TPGME Fuel Additive

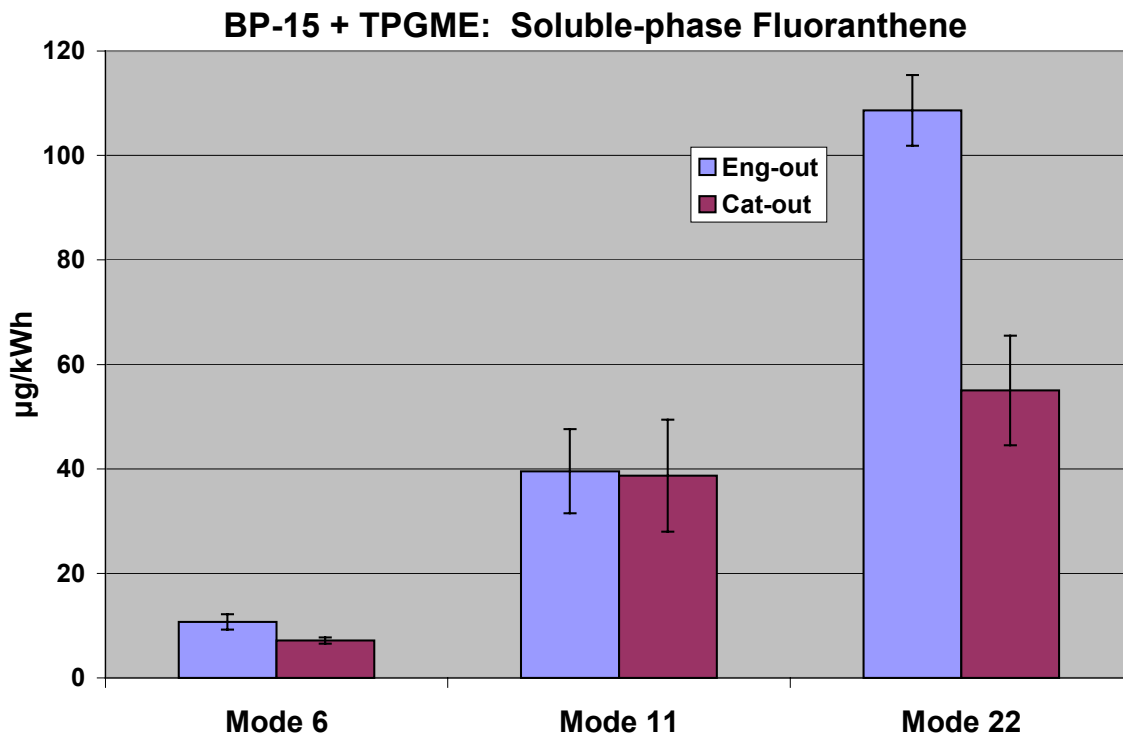


Figure G-39. Soluble-Phase Fluoranthene Emissions with TPGME Fuel Additive

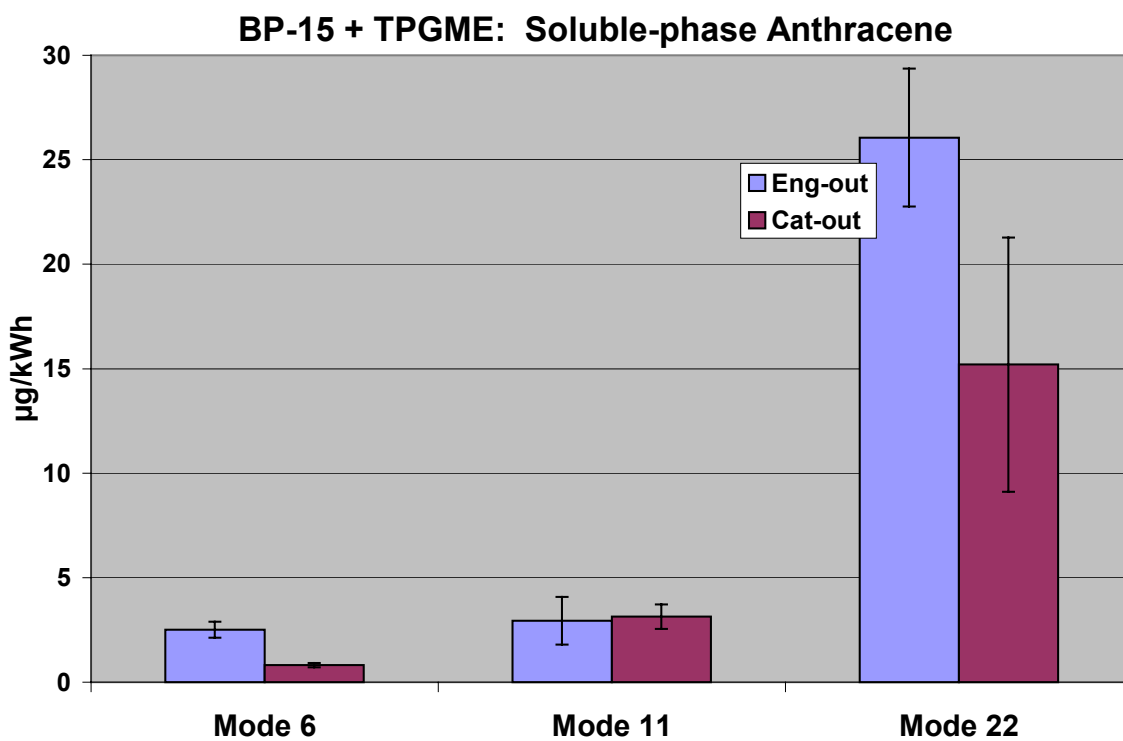


Figure G-40. Soluble-Phase Anthracene Emissions with TPGME Fuel Additive

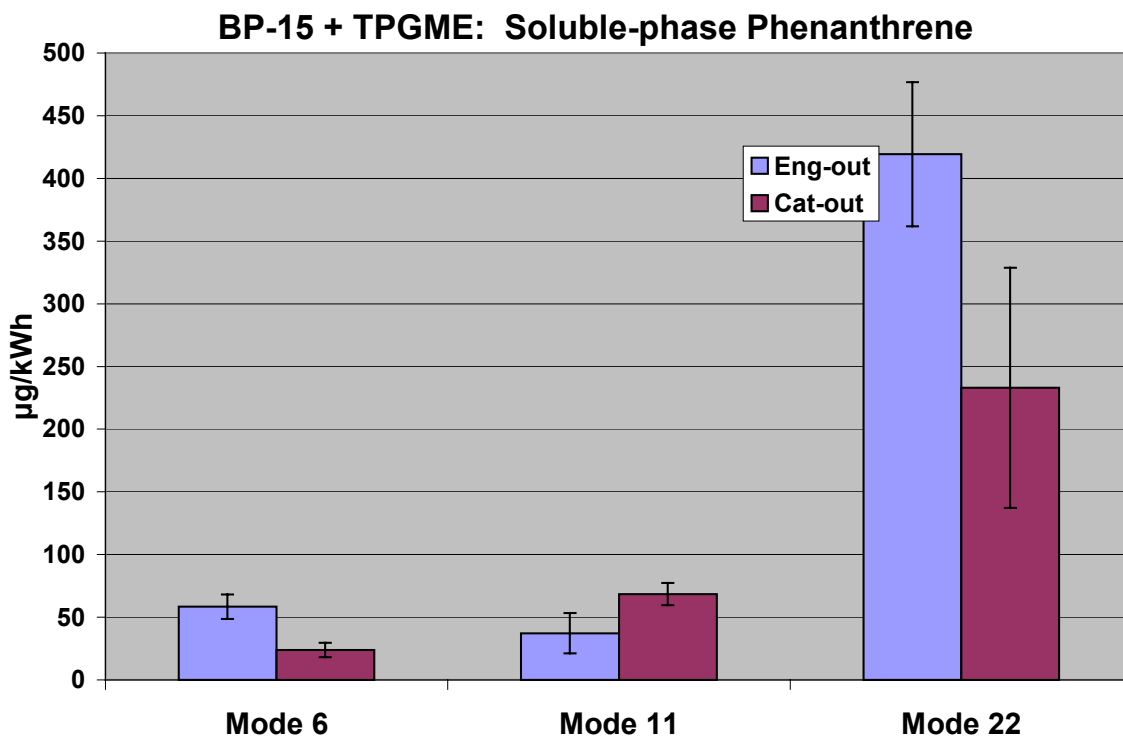


Figure G-41. Soluble-Phase Phenanthrene Emissions with TPGME Fuel Additive

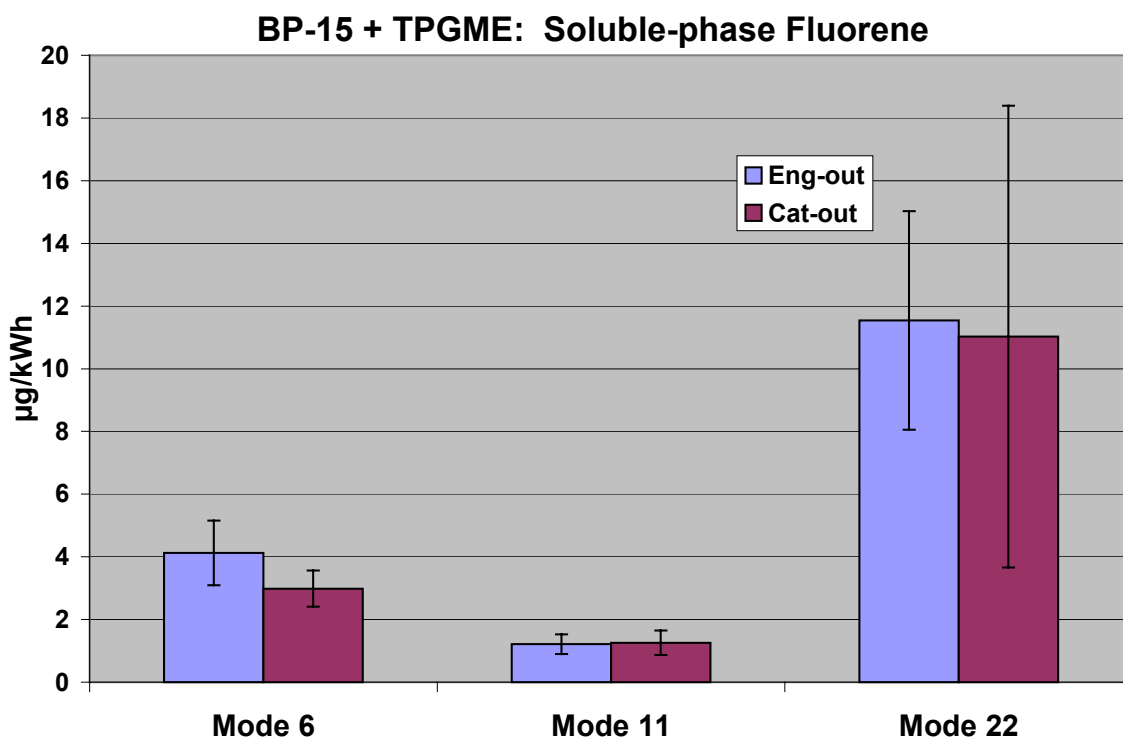


Figure G-42. Soluble-Phase Fluorene Emissions with TPGME Fuel Additive

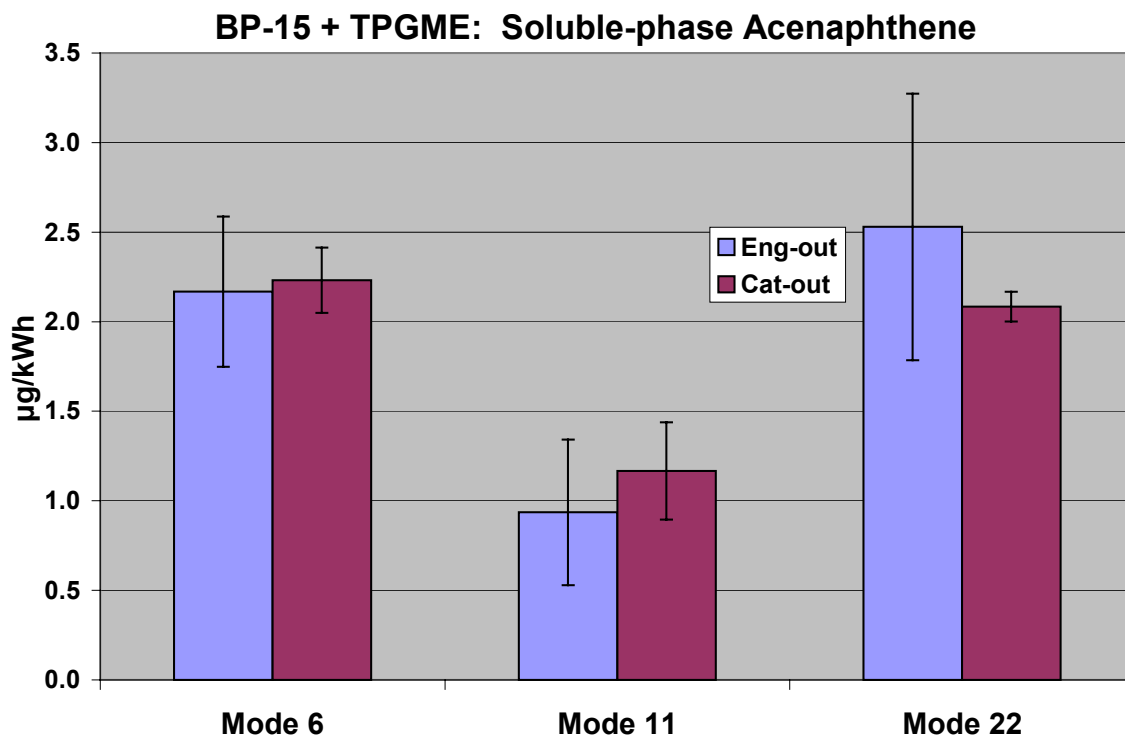


Figure G-43. Soluble-Phase Acenaphthene Emissions with TPGME Fuel Additive

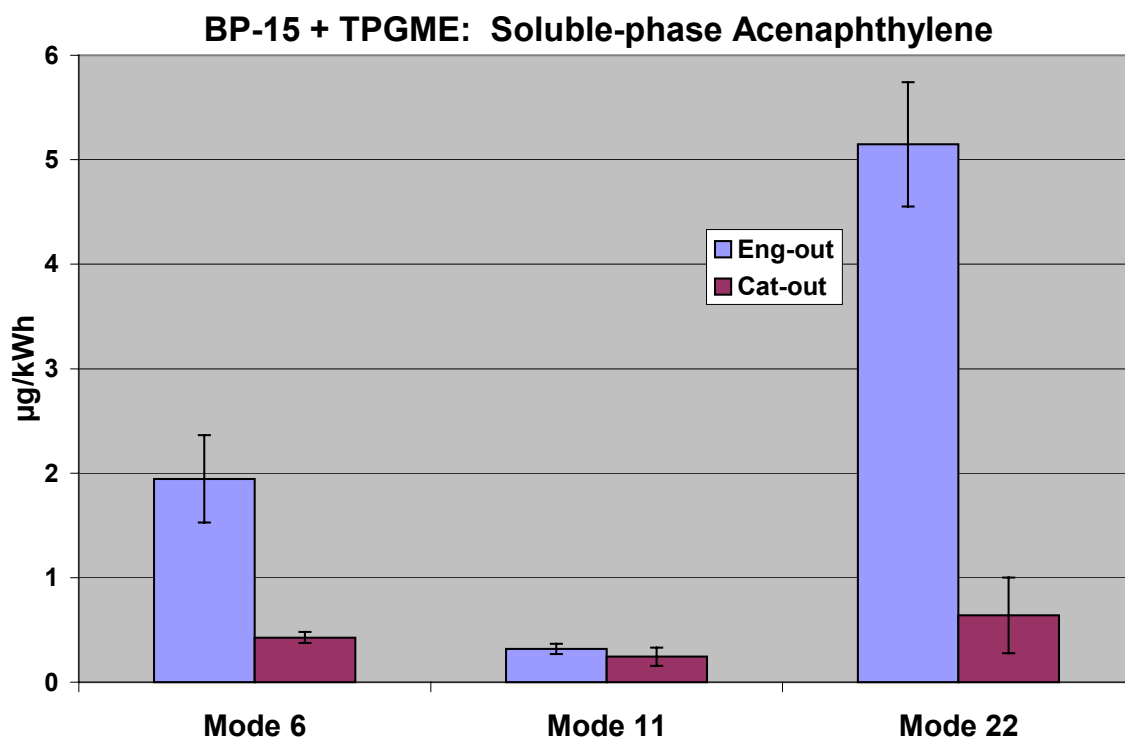


Figure G-44. Soluble-Phase Acenaphthylene Emissions with TPGME Fuel Additive

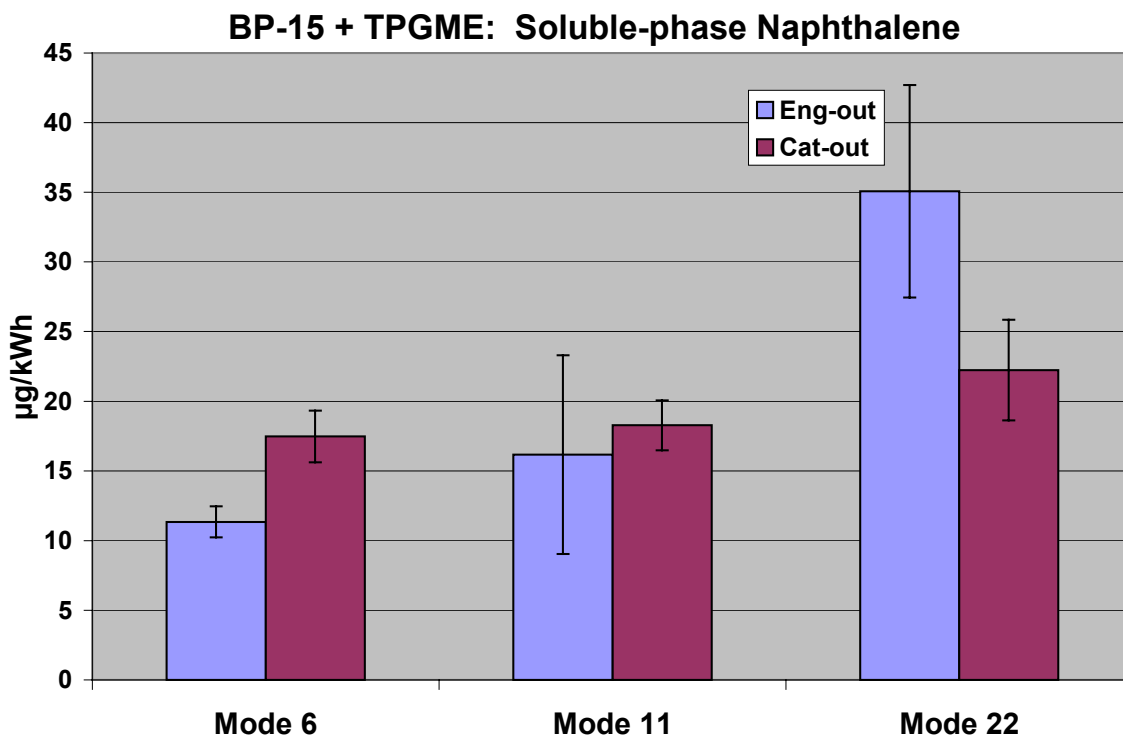


Figure G-45. Soluble-Phase Naphthalene Emissions with TPGME Fuel Additive

## **APPENDIX H**

### **FT100 Fuel Operation Test Results**



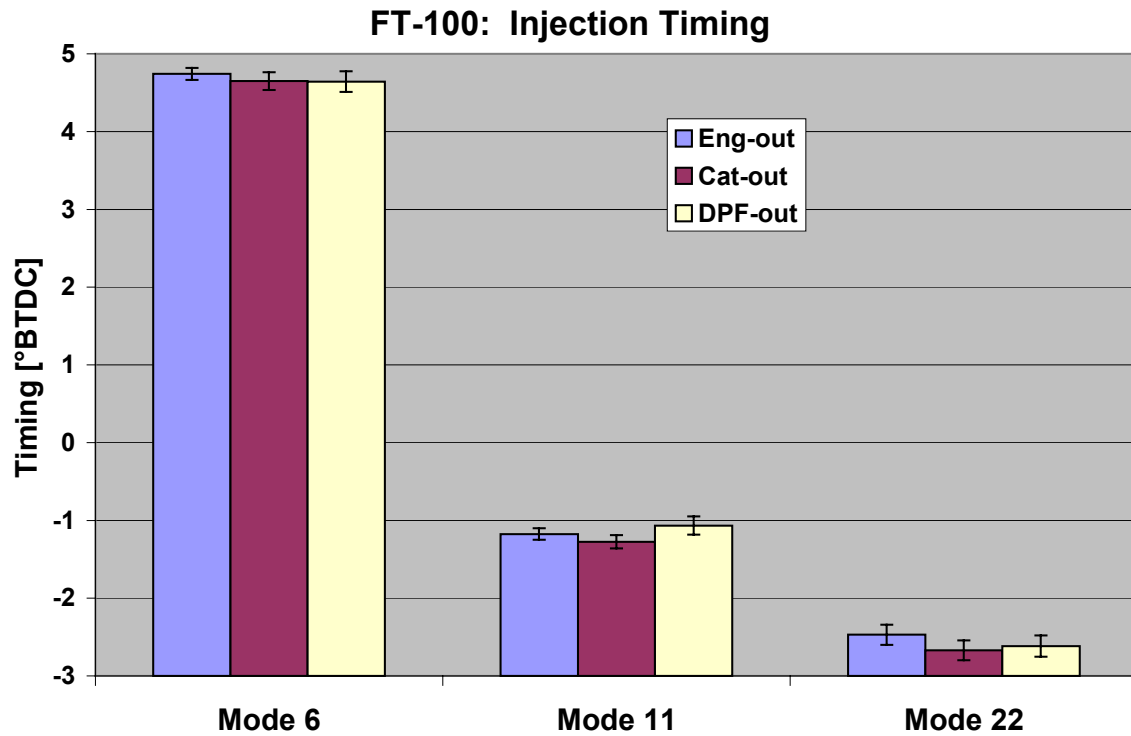


Figure H-1. Injection Timing with Fischer-Tropsch Fuel

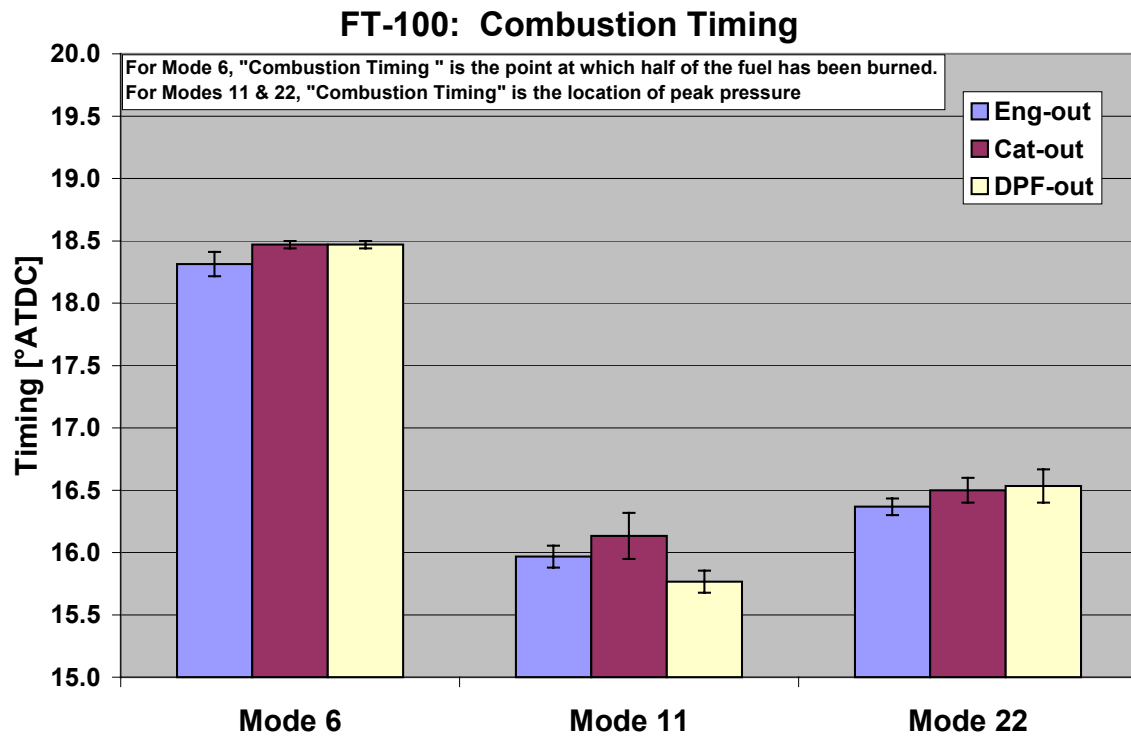


Figure H-2. Combustion Timing with Fischer-Tropsch Fuel

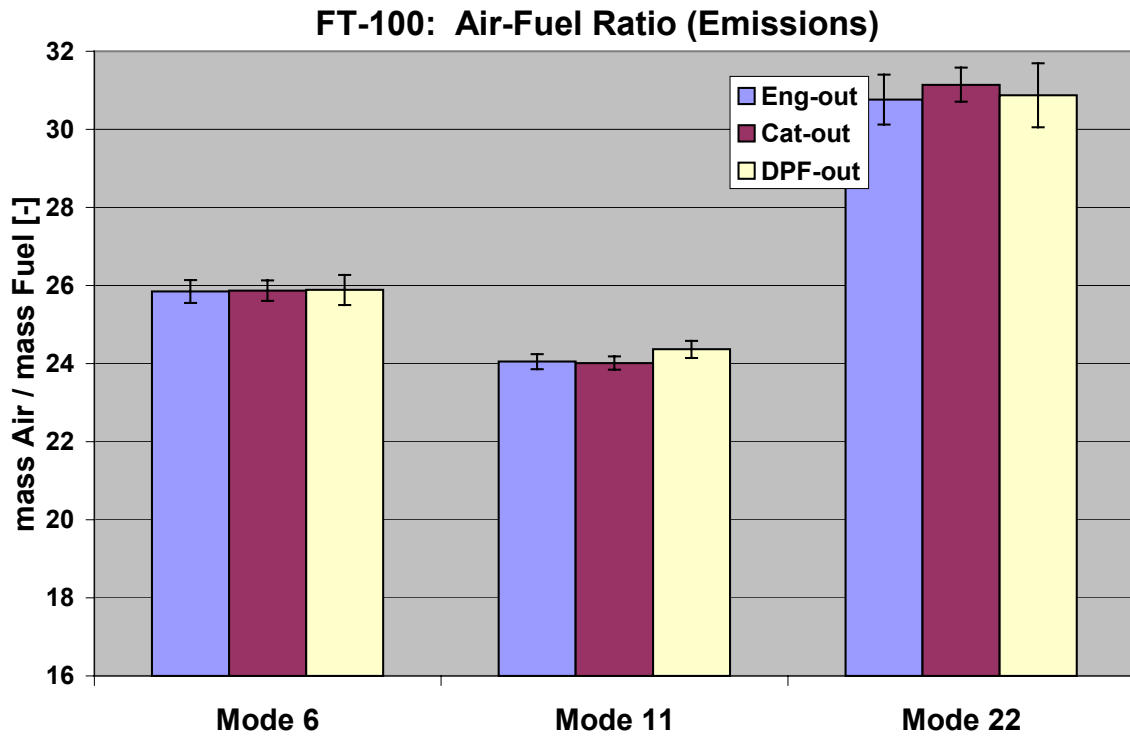


Figure H-3. Emissions Air-Fuel Ratio with Fischer-Tropsch Fuel

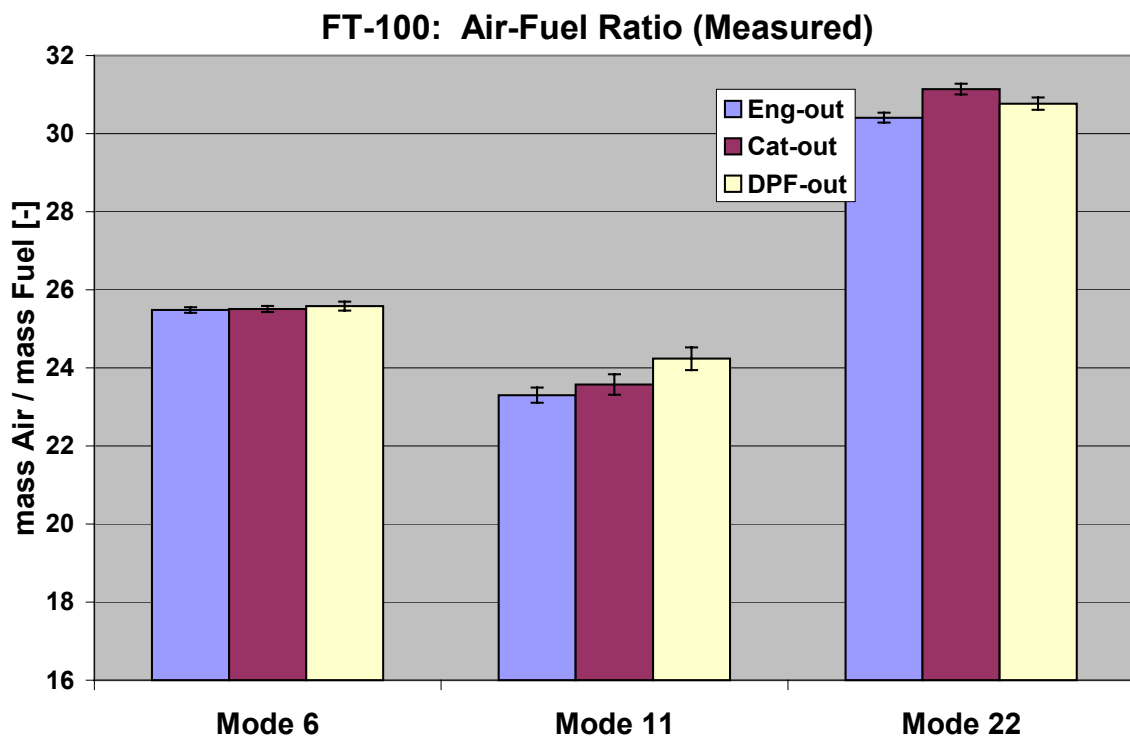


Figure H-4. Measured Air-Fuel Ratio with Fischer-Tropsch Fuel

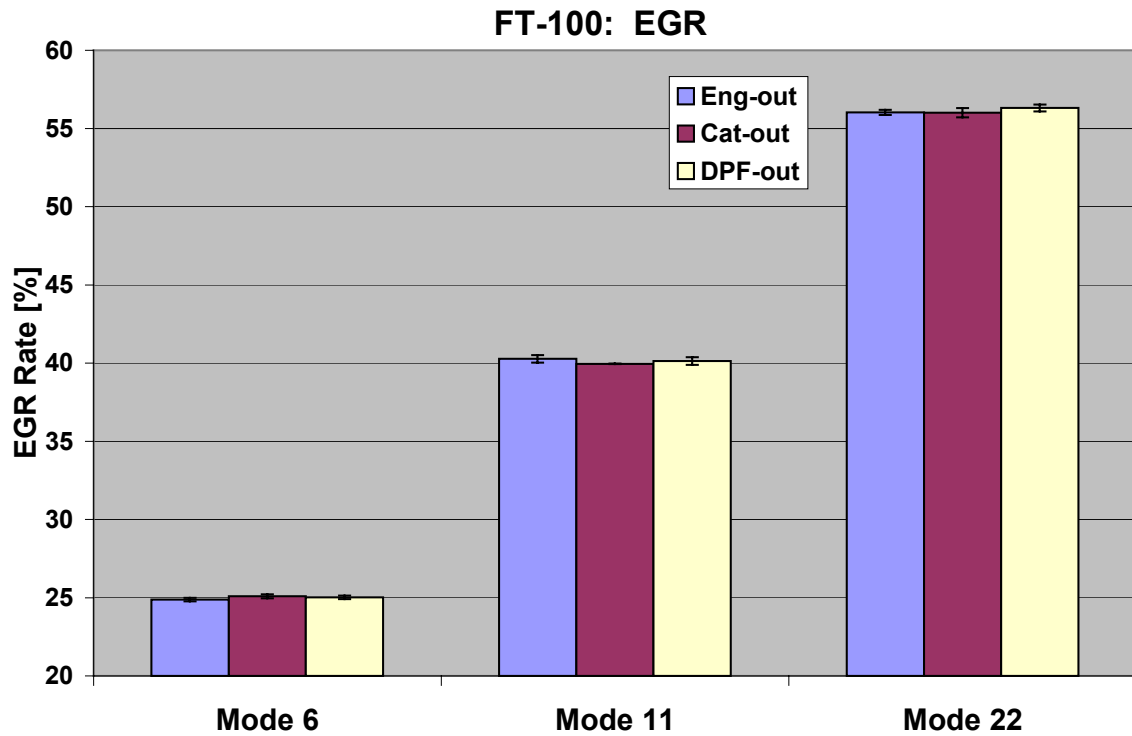


Figure H-5. EGR Rate with Fischer-Tropsch Fuel

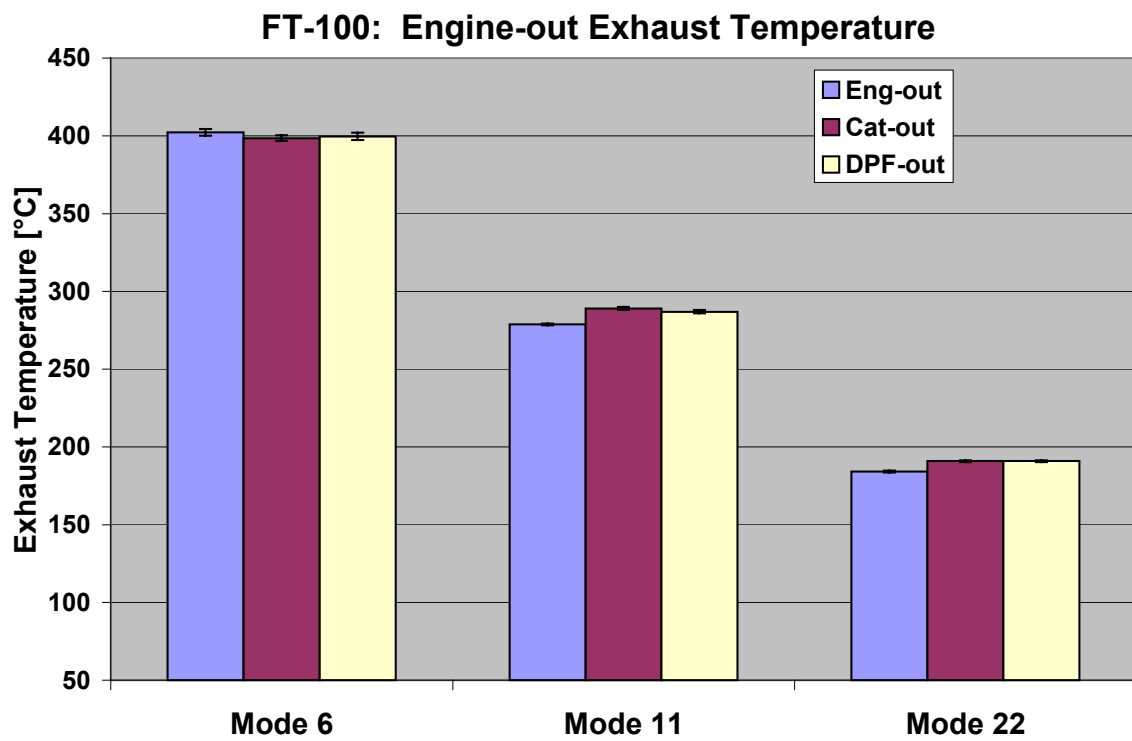


Figure H-6. Engine-Out Exhaust Temperature with Fischer-Tropsch Fuel

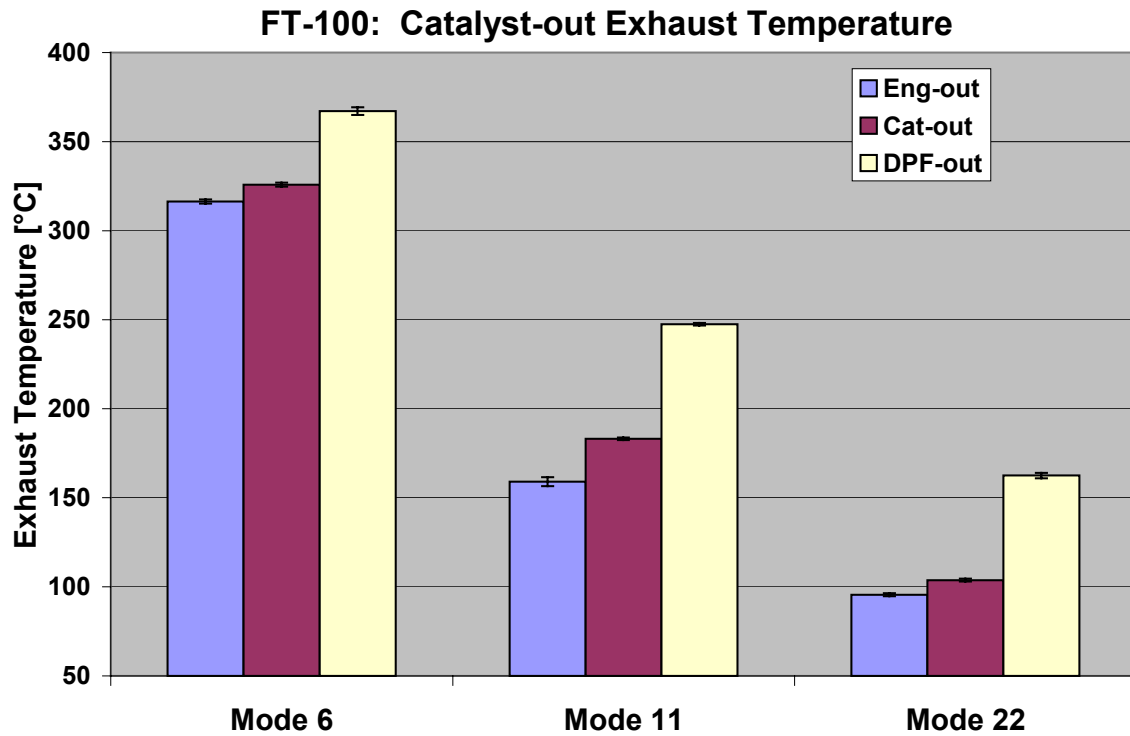


Figure H-7. Catalyst-Out Exhaust Temperature with Fischer-Tropsch Fuel

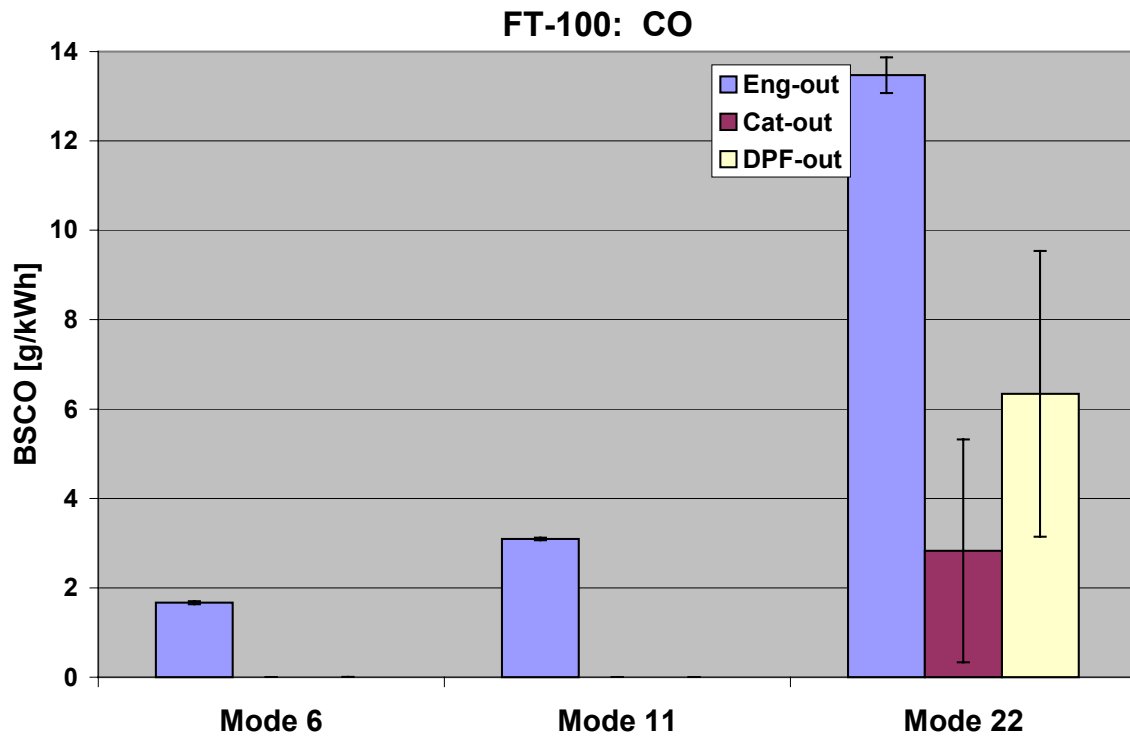


Figure H-8. Carbon Monoxide Emissions with Fischer-Tropsch Fuel

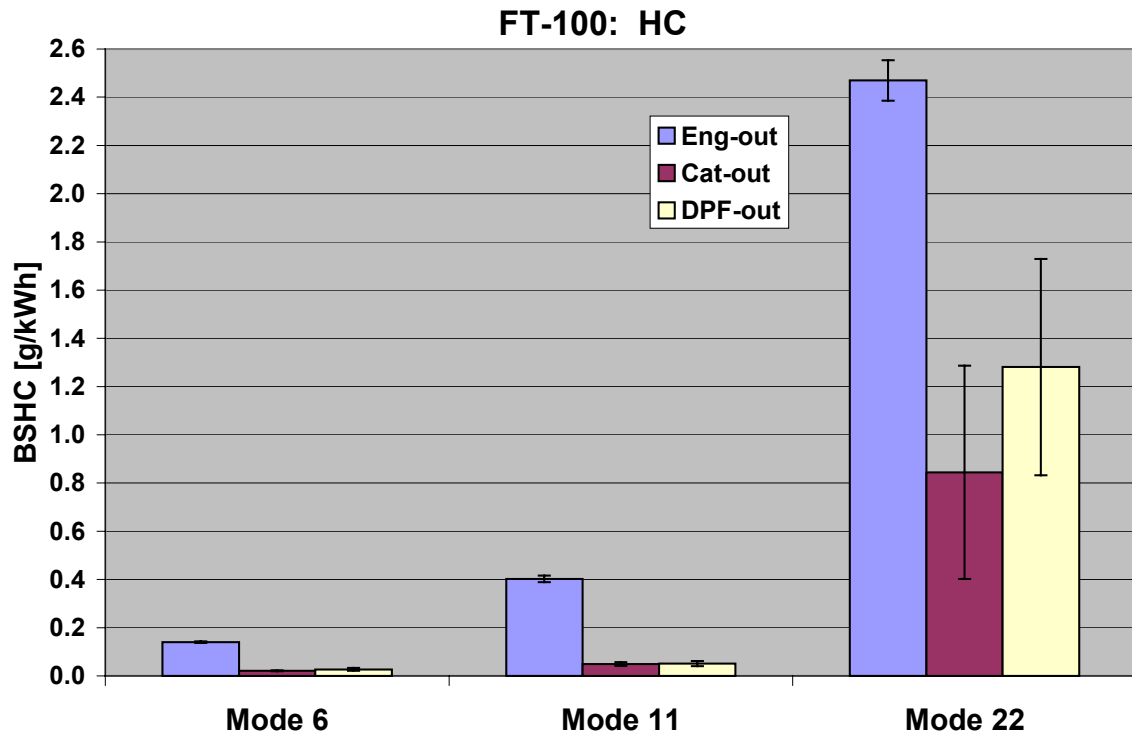


Figure H-9. Hydrocarbon Emissions with Fischer-Tropsch Fuel

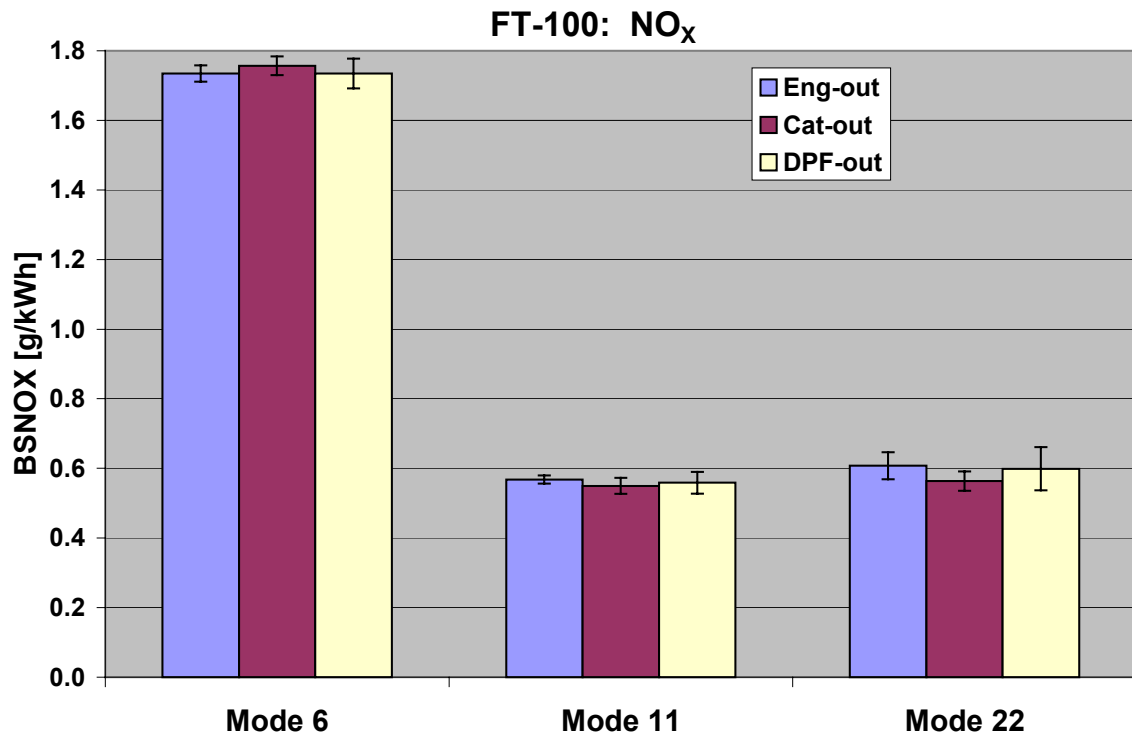


Figure H-10. Nitrogen Oxides Emissions with Fischer-Tropsch Fuel

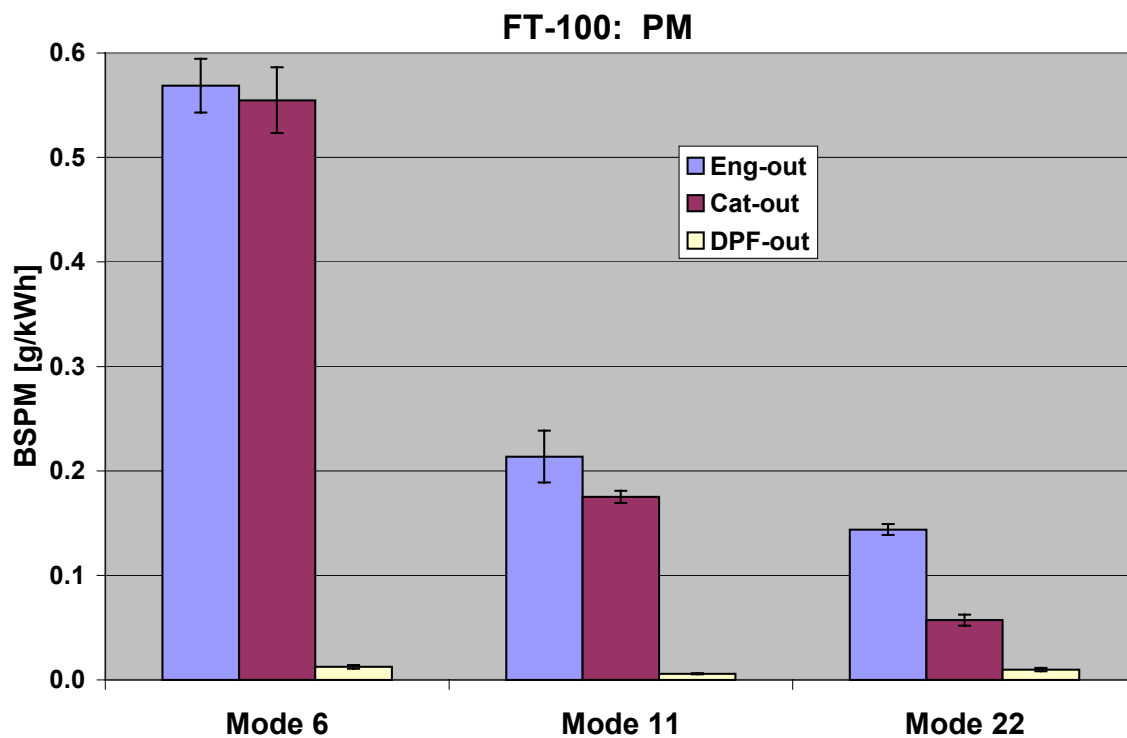


Figure H-11. Particulate Matter Emissions with Fischer-Tropsch Fuel

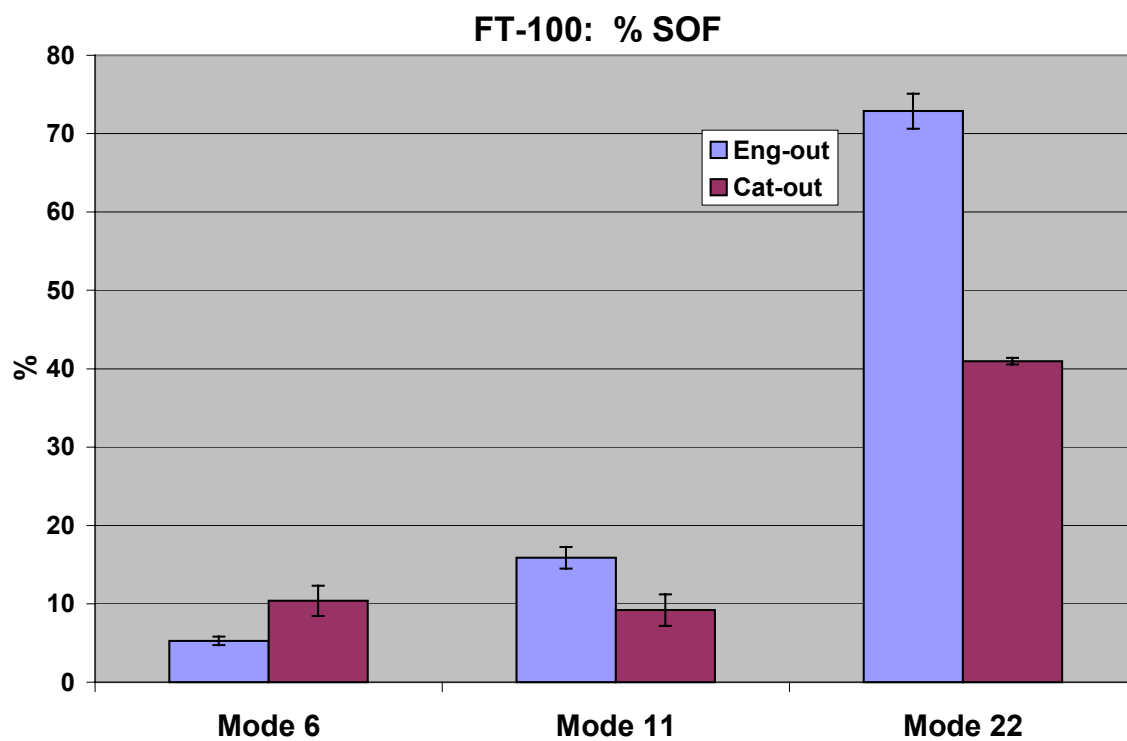


Figure H-12. Percent Soluble Organic Fraction with Fischer-Tropsch Fuel

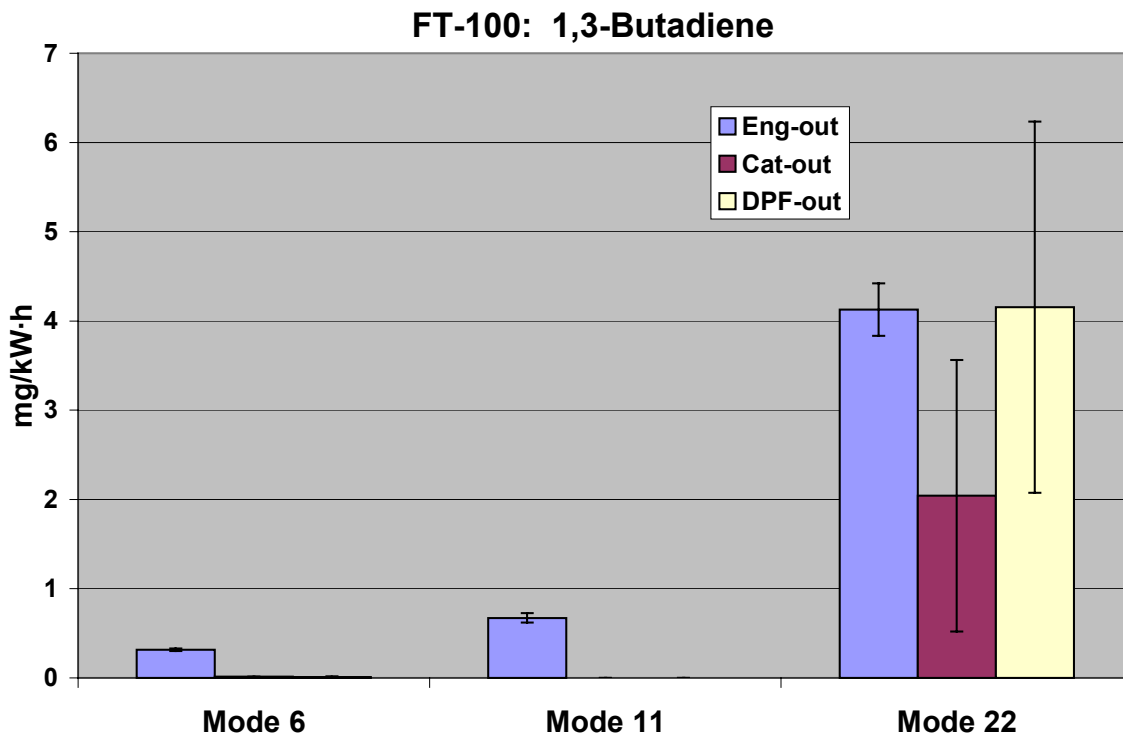


Figure H-13. 1,3-Butadiene Emissions with Fischer-Tropsch Fuel

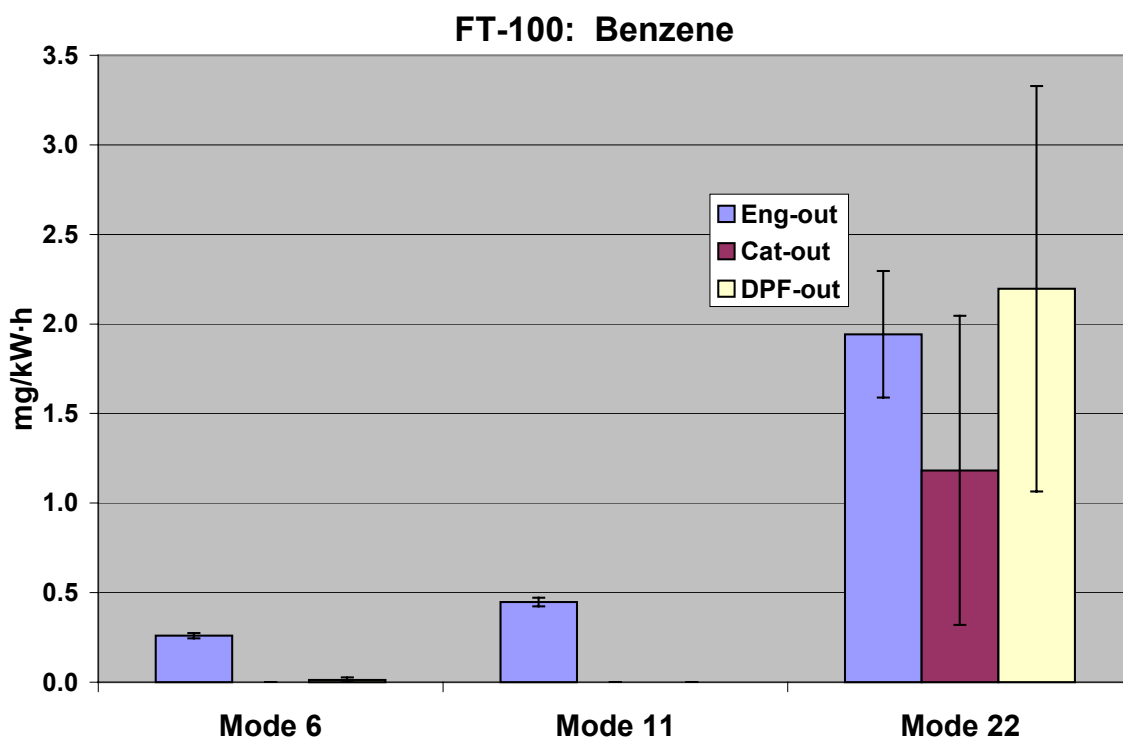


Figure H-14. Benzene Emissions with Fischer-Tropsch Fuel

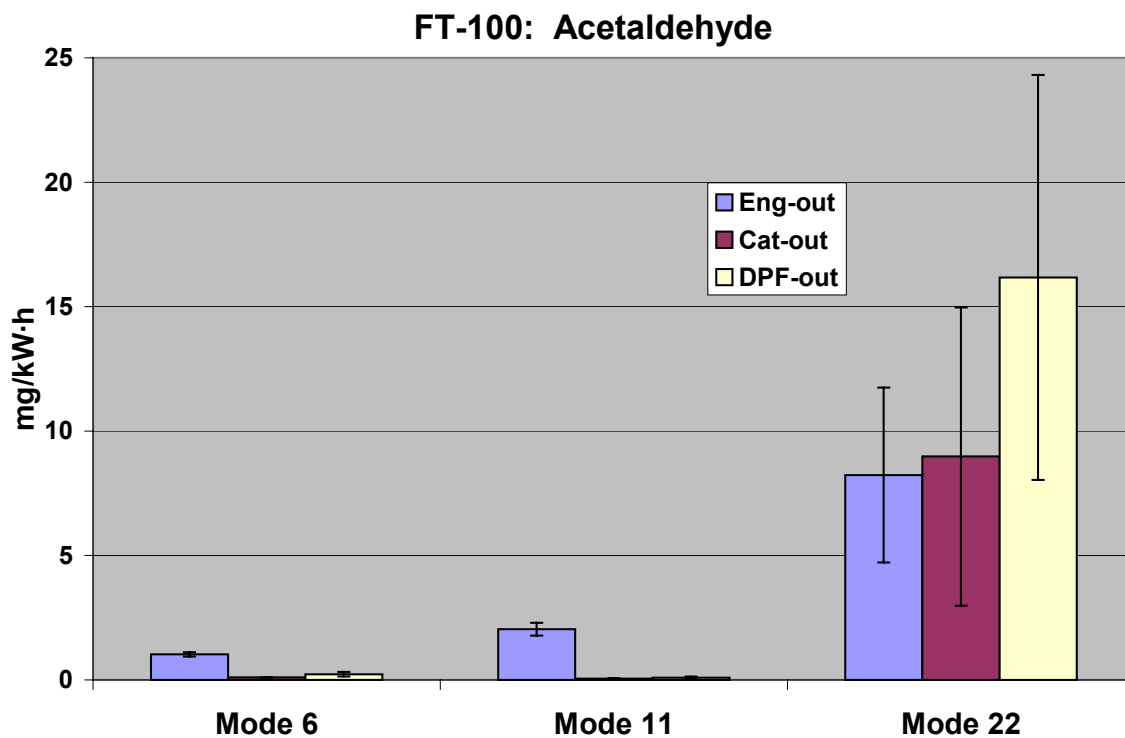


Figure H-15. Acetaldehyde Emissions with Fischer-Tropsch Fuel

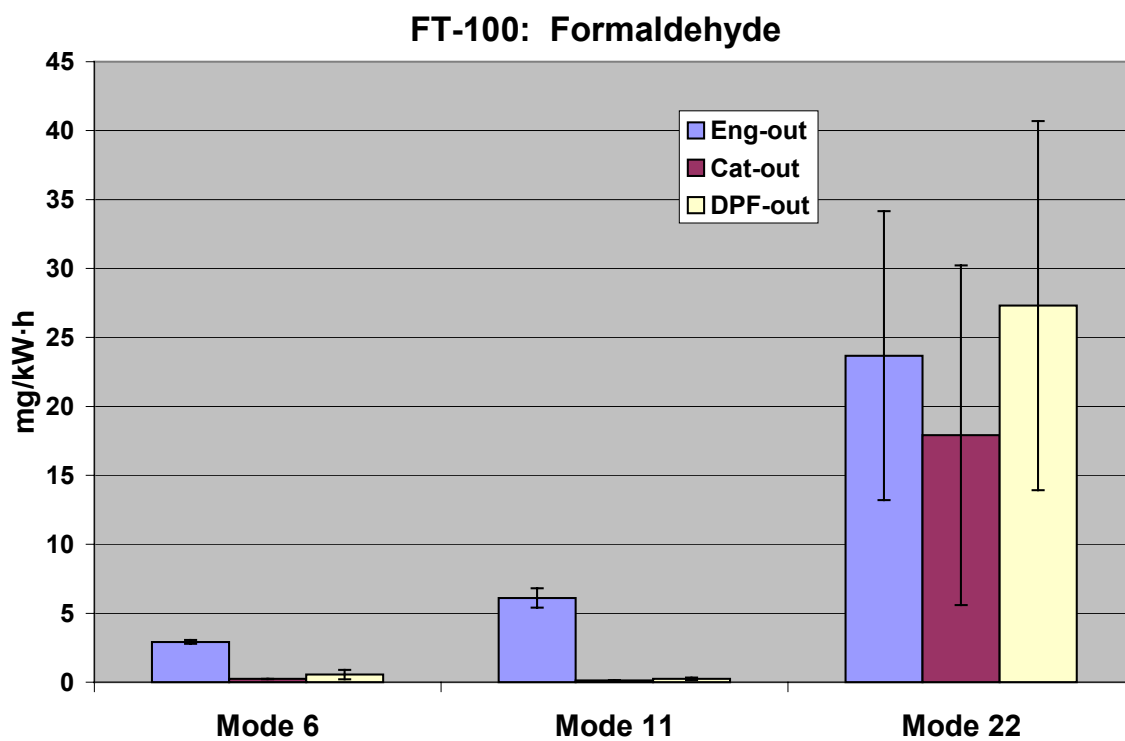


Figure H-16. Formaldehyde Emissions with Fischer-Tropsch Fuel



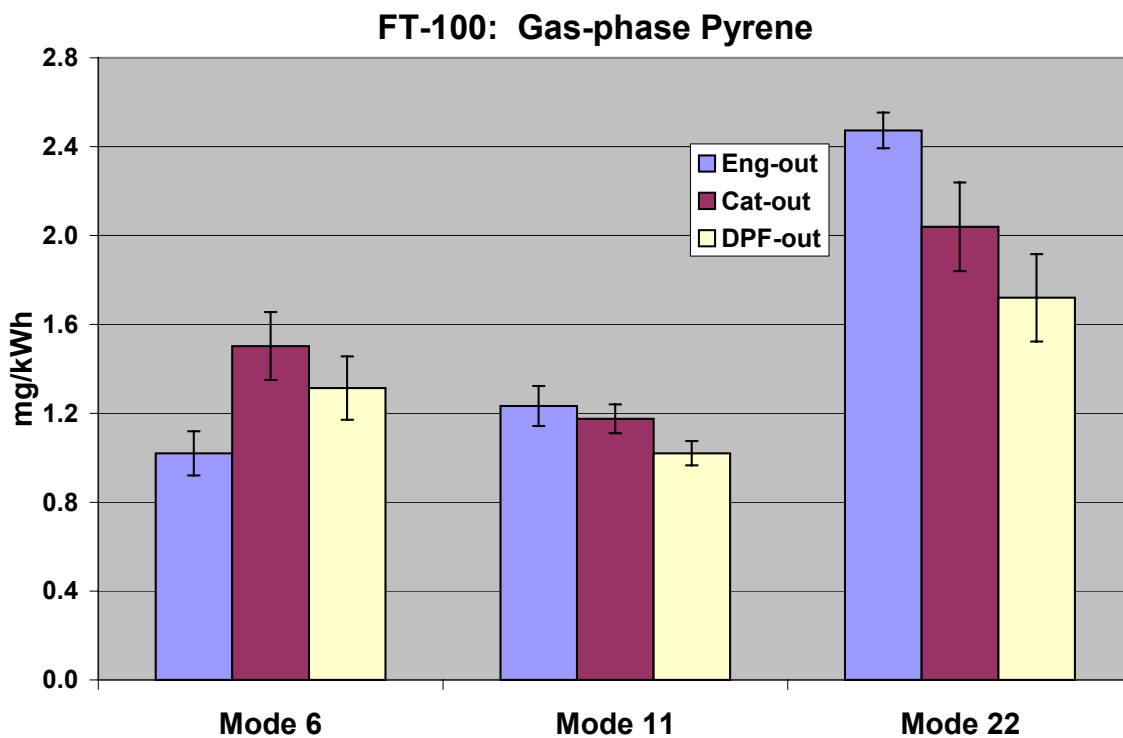


Figure H-17. Gas-Phase Pyrene Emissions with Fischer-Tropsch Fuel

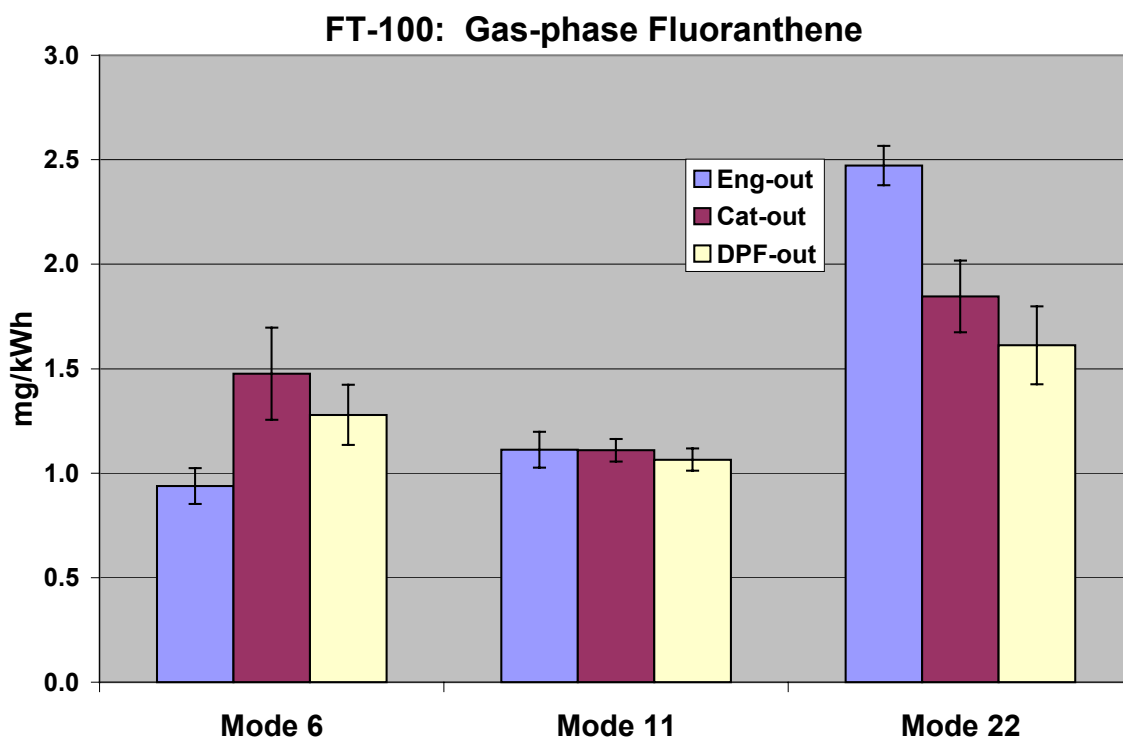


Figure H-18. Gas-Phase Fluoranthene Emissions with Fischer-Tropsch Fuel

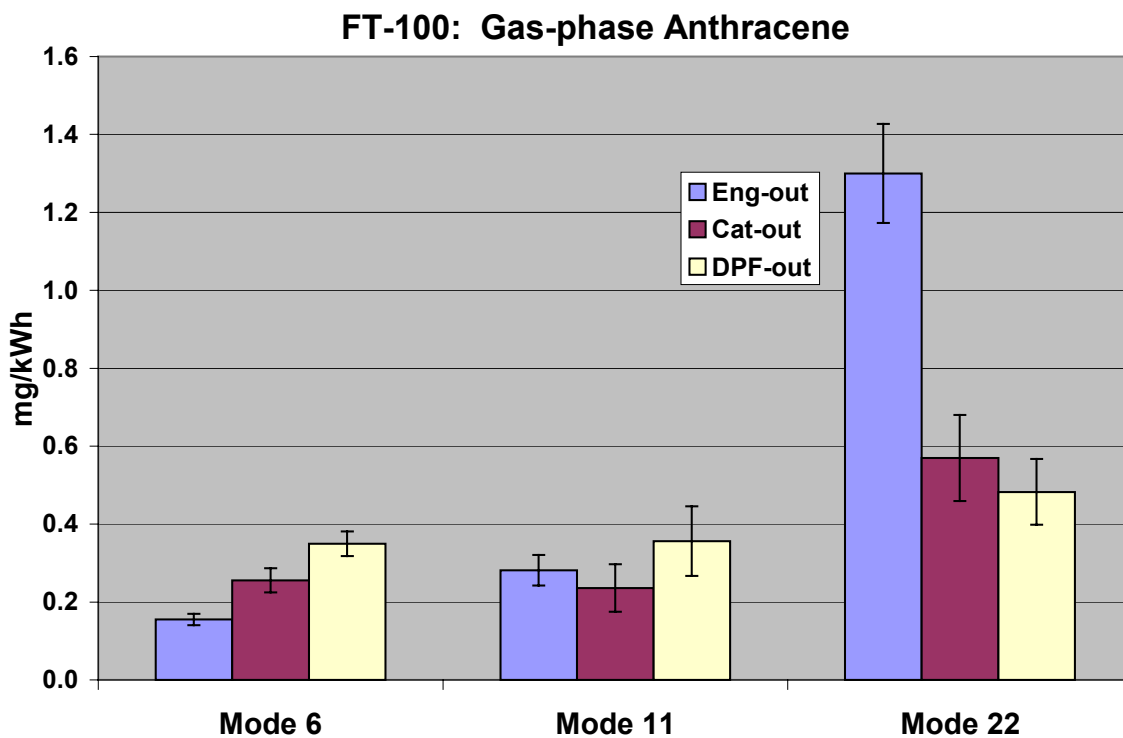


Figure H-19. Gas-Phase Anthracene Emissions with Fischer-Tropsch Fuel

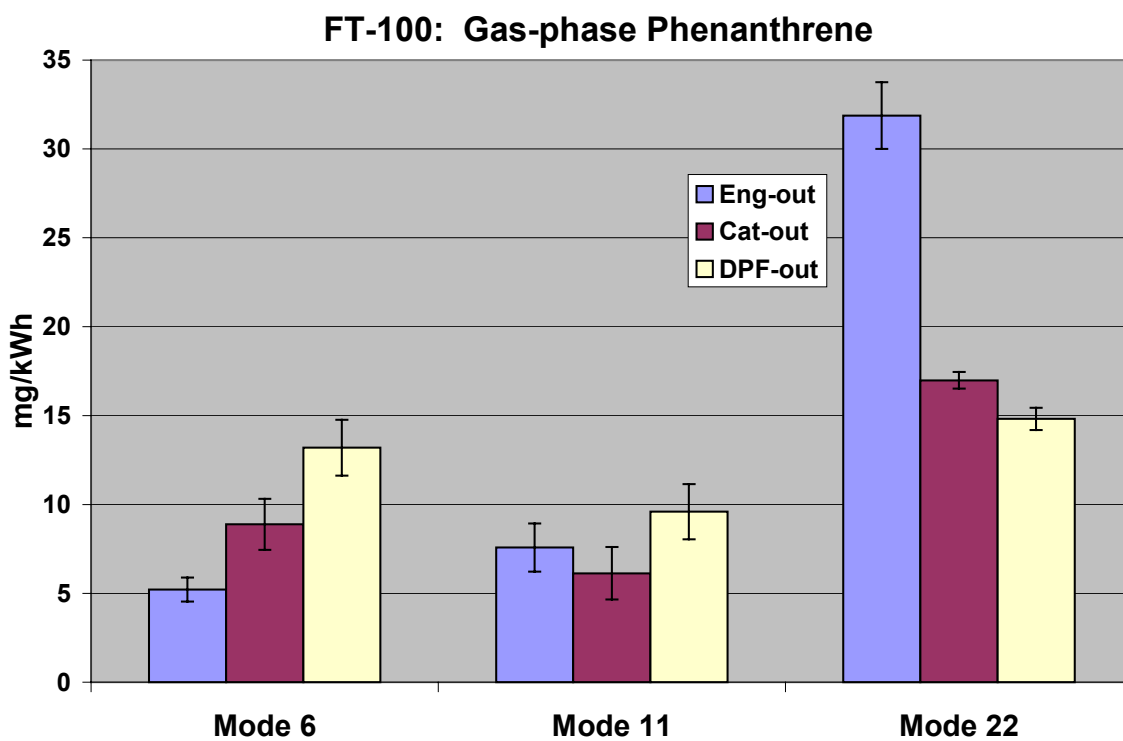


Figure H-20. Gas-Phase Phenanthrene Emissions with Fischer-Tropsch Fuel

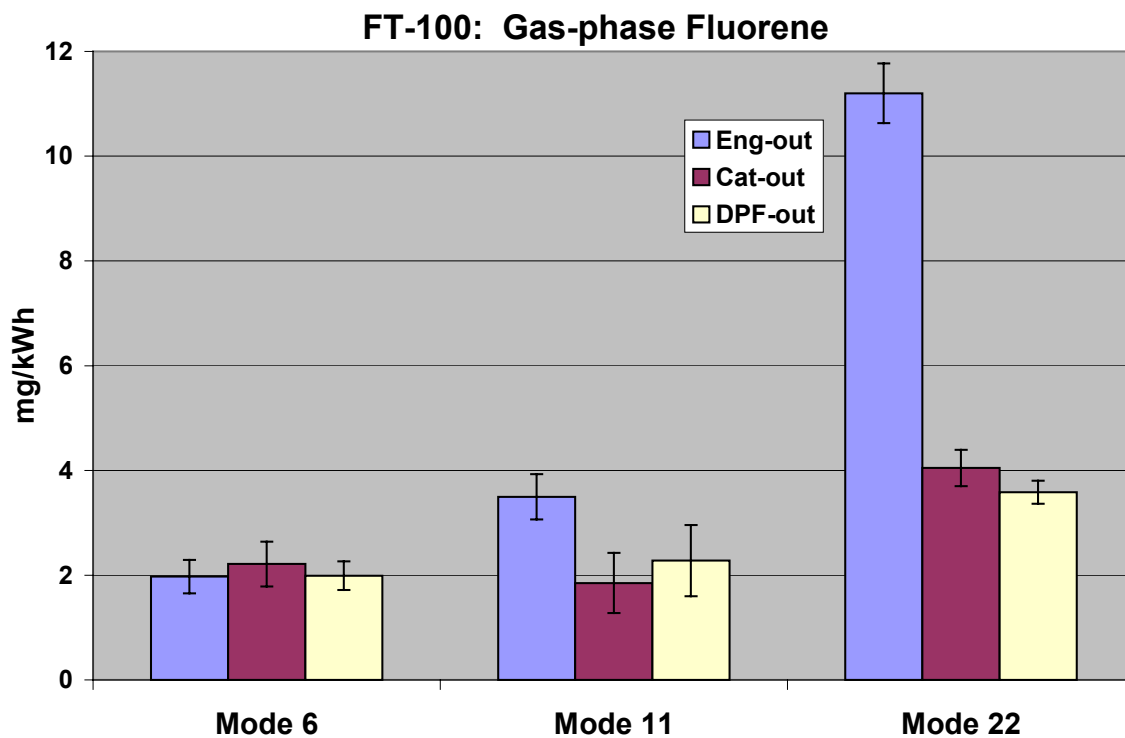


Figure H-21. Gas-Phase Fluorene Emissions with Fischer-Tropsch Fuel

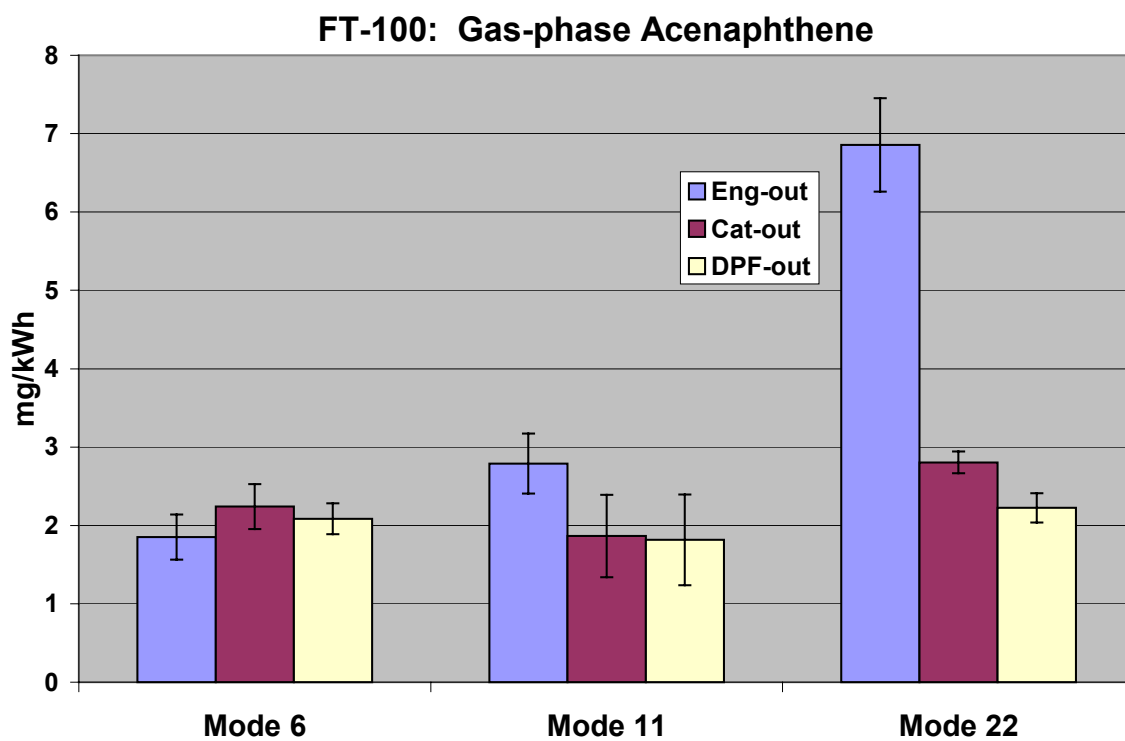


Figure H-22. Gas-Phase Acenaphthene Emissions with Fischer-Tropsch Fuel

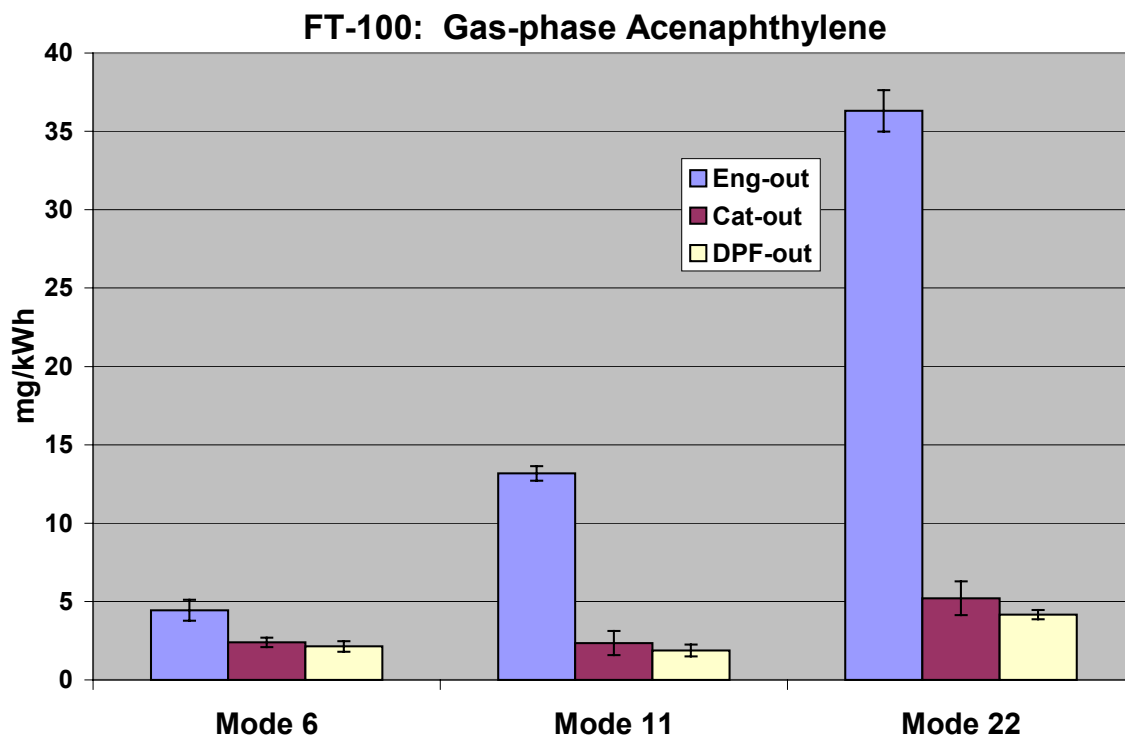


Figure H-23. Gas-Phase Acenaphthylene Emissions with Fischer-Tropsch Fuel

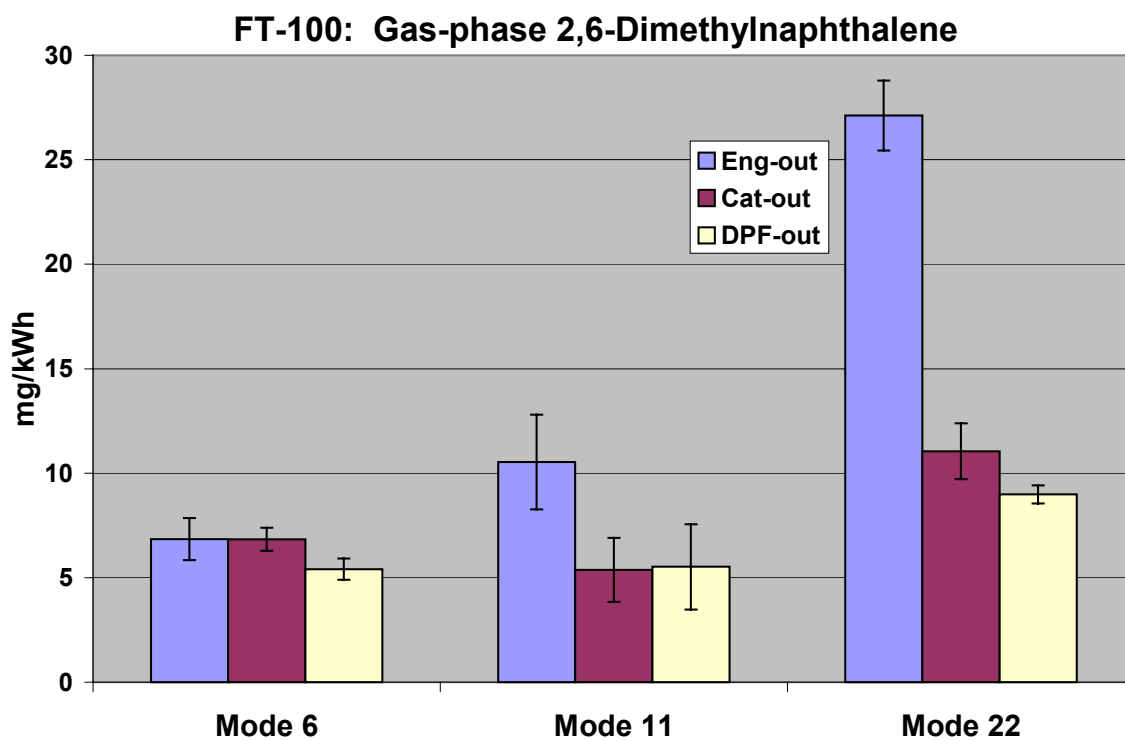


Figure H-24. Gas-Phase 2,6-Dimethylnaphthalene Emissions with Fischer-Tropsch Fuel

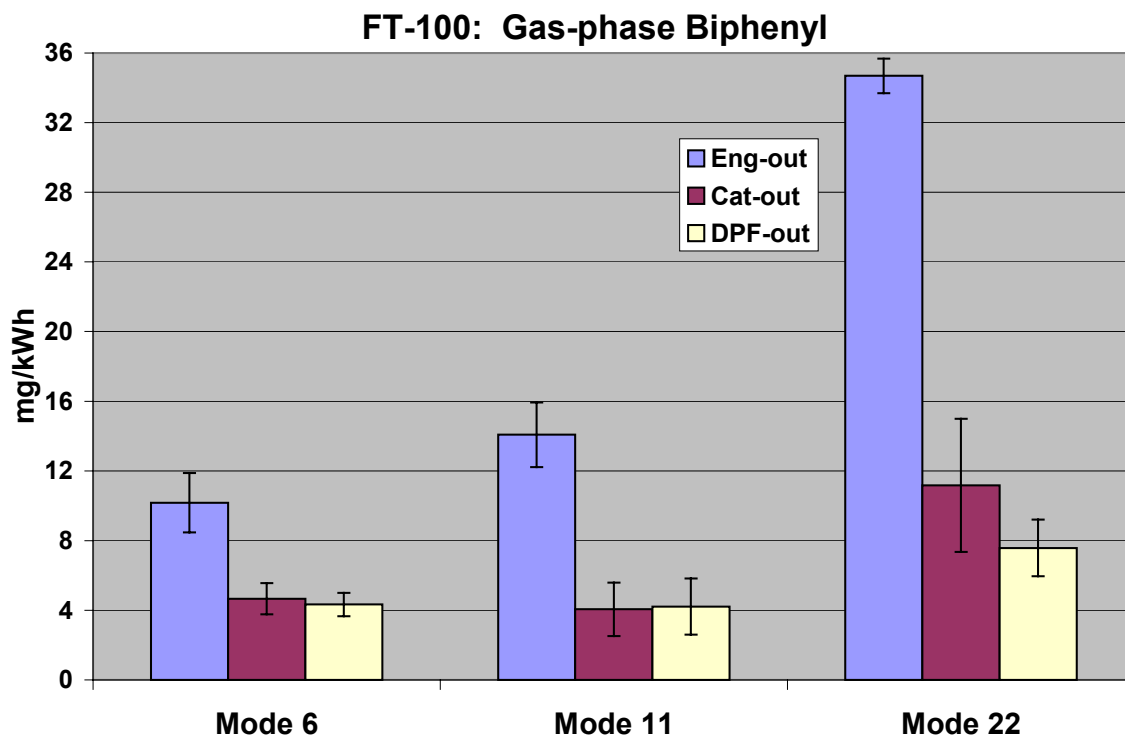


Figure H-25. Gas-Phase Biphenyl Emissions with Fischer-Tropsch Fuel

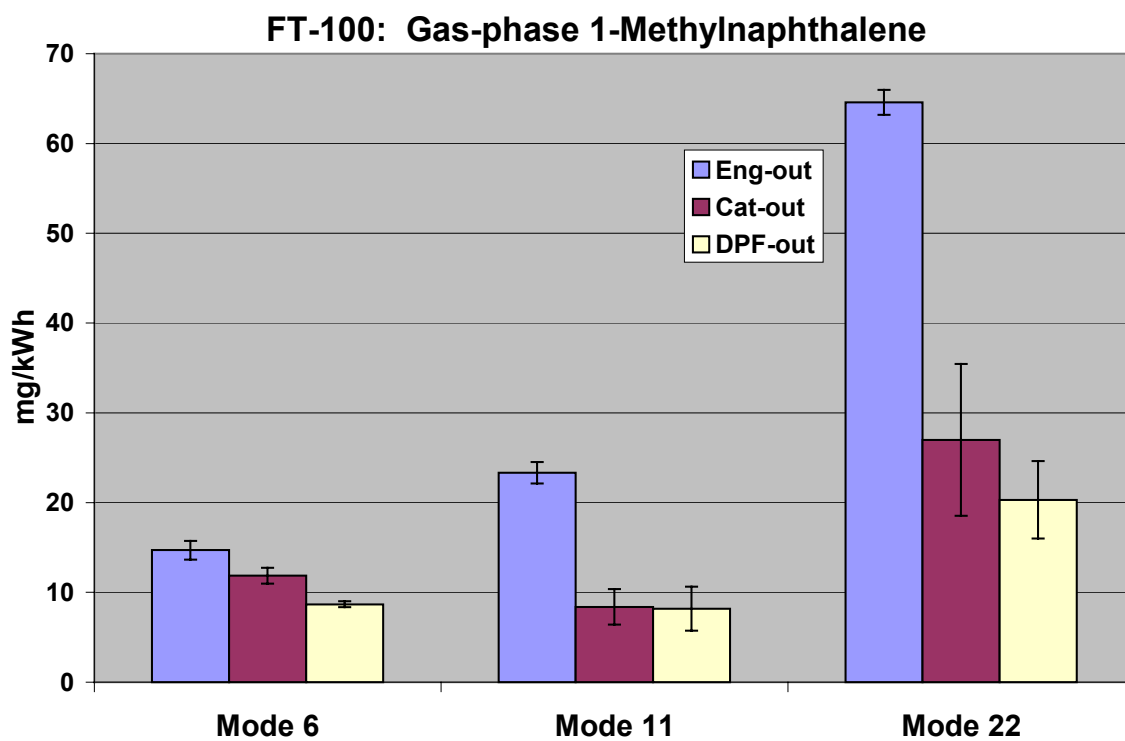


Figure H-26. Gas-Phase 1-Methylnaphthalene Emissions with Fischer-Tropsch Fuel

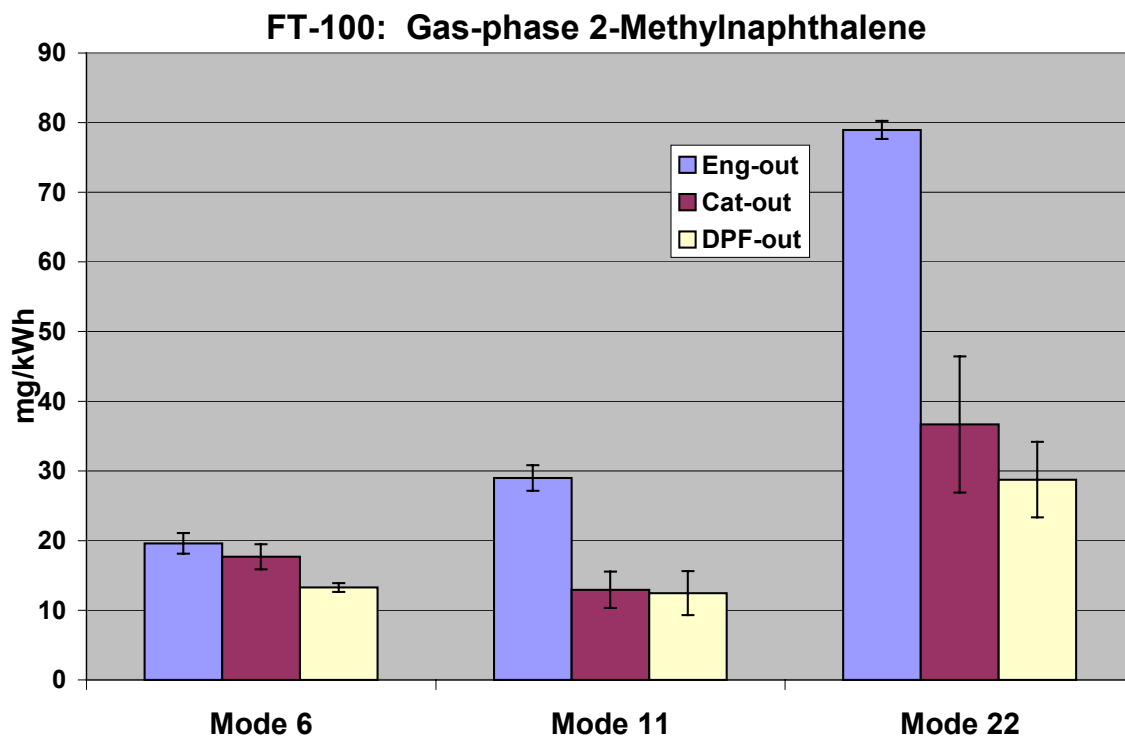


Figure H-27. Gas-Phase 2-Methylnaphthalene Emissions with Fischer-Tropsch Fuel

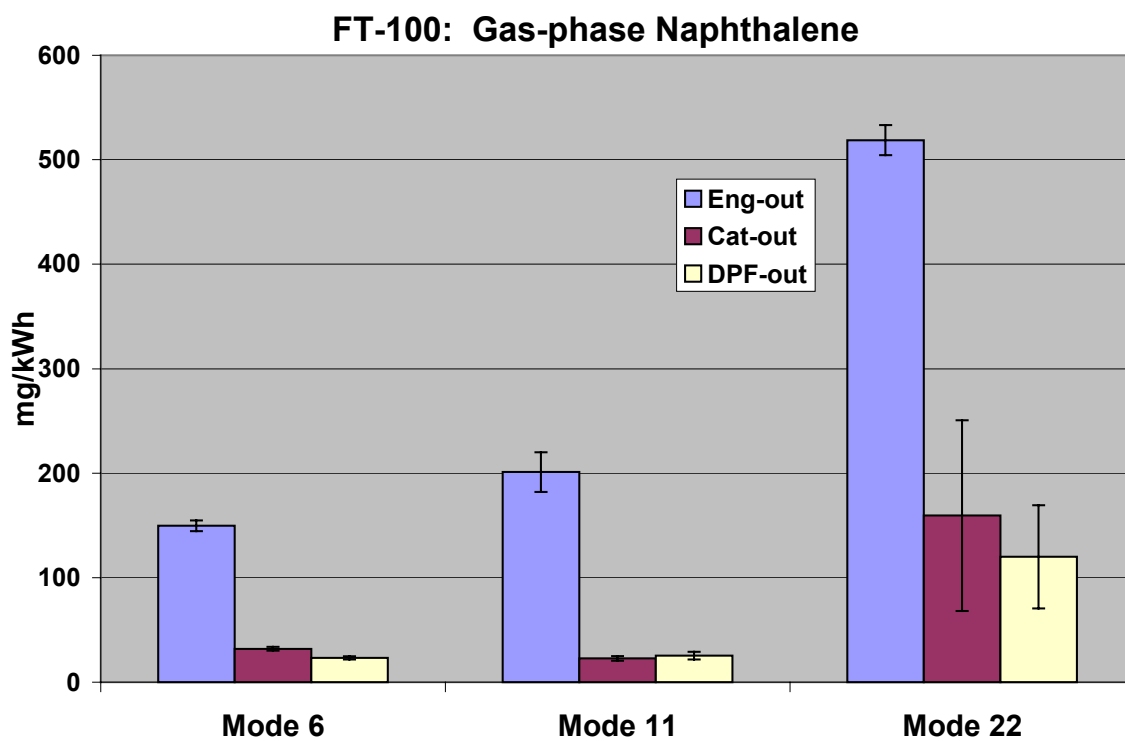


Figure H-28. Gas-Phase Naphthalene Emissions with Fischer-Tropsch Fuel

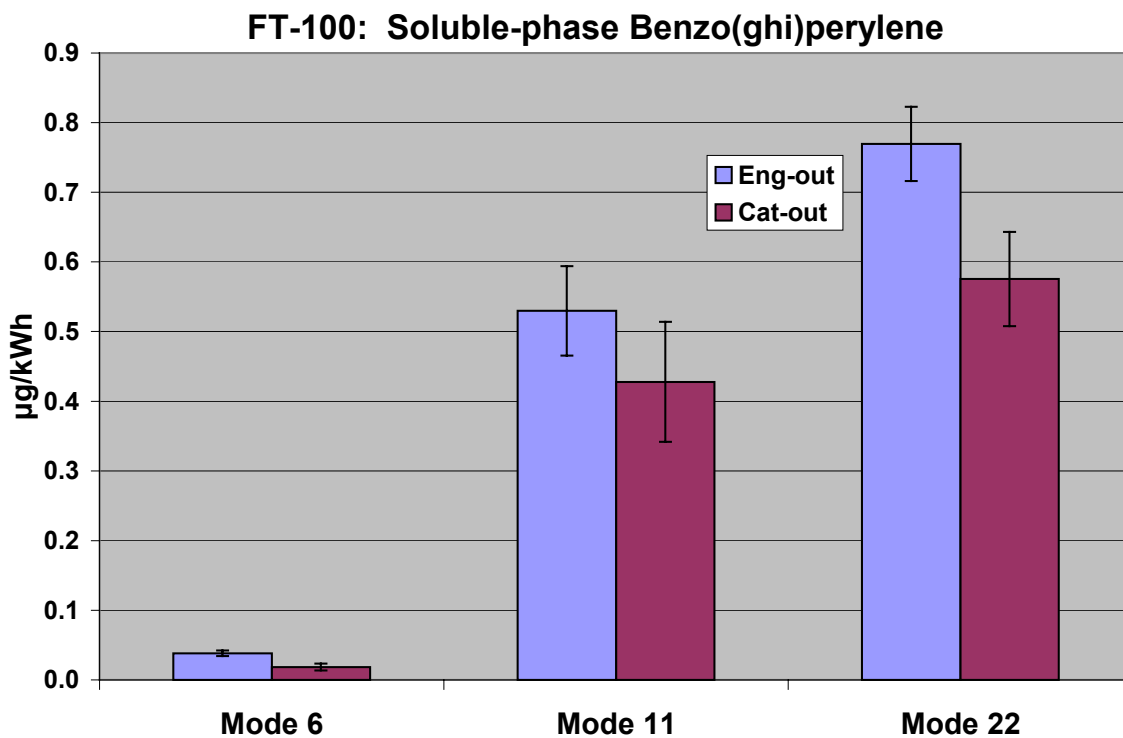


Figure H-29. Soluble-Phase Benzo(ghi)perylene Emissions with Fischer-Tropsch Fuel

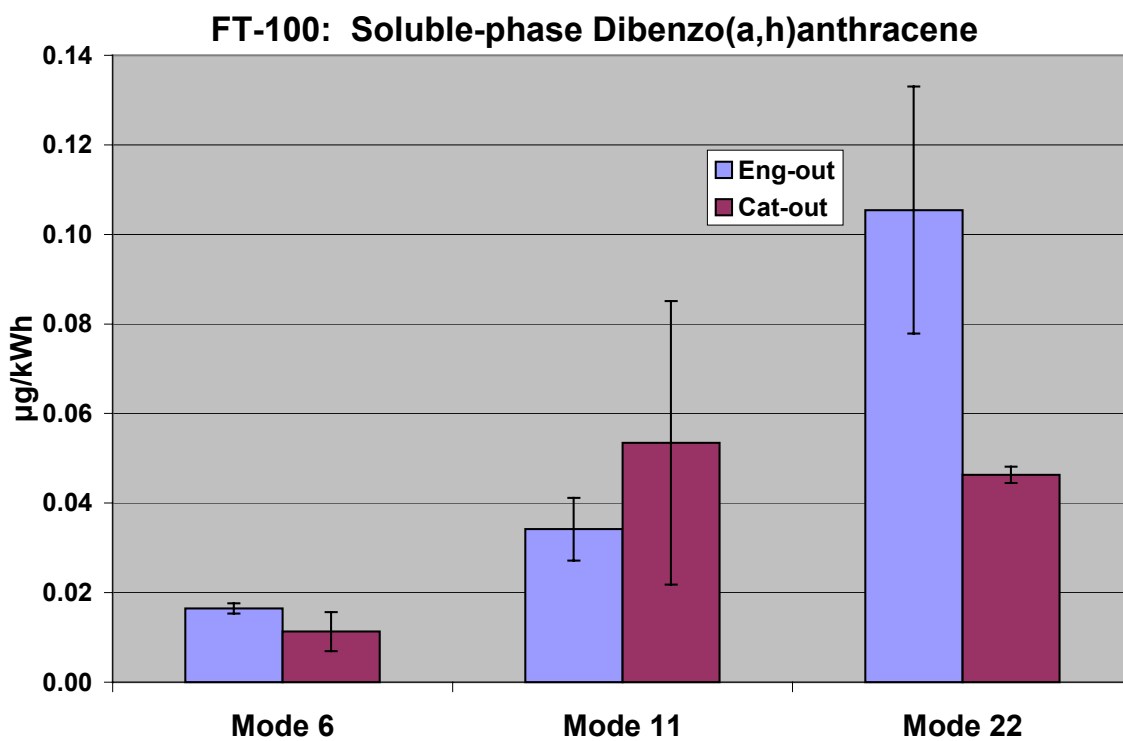


Figure H-30. Soluble-Phase Dibenzo(a,h)anthracene Emissions with Fischer-Tropsch Fuel

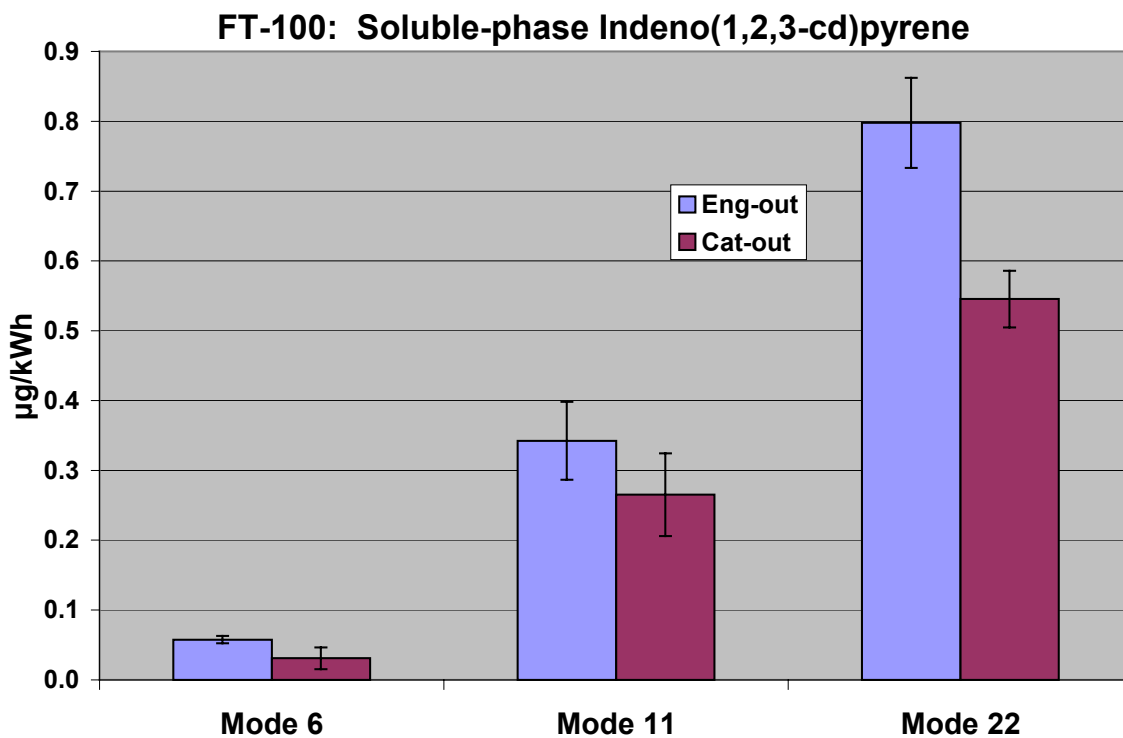


Figure H-31. Soluble-Phase Indeno(1,2,3-cd)pyrene Emissions with Fischer-Tropsch Fuel

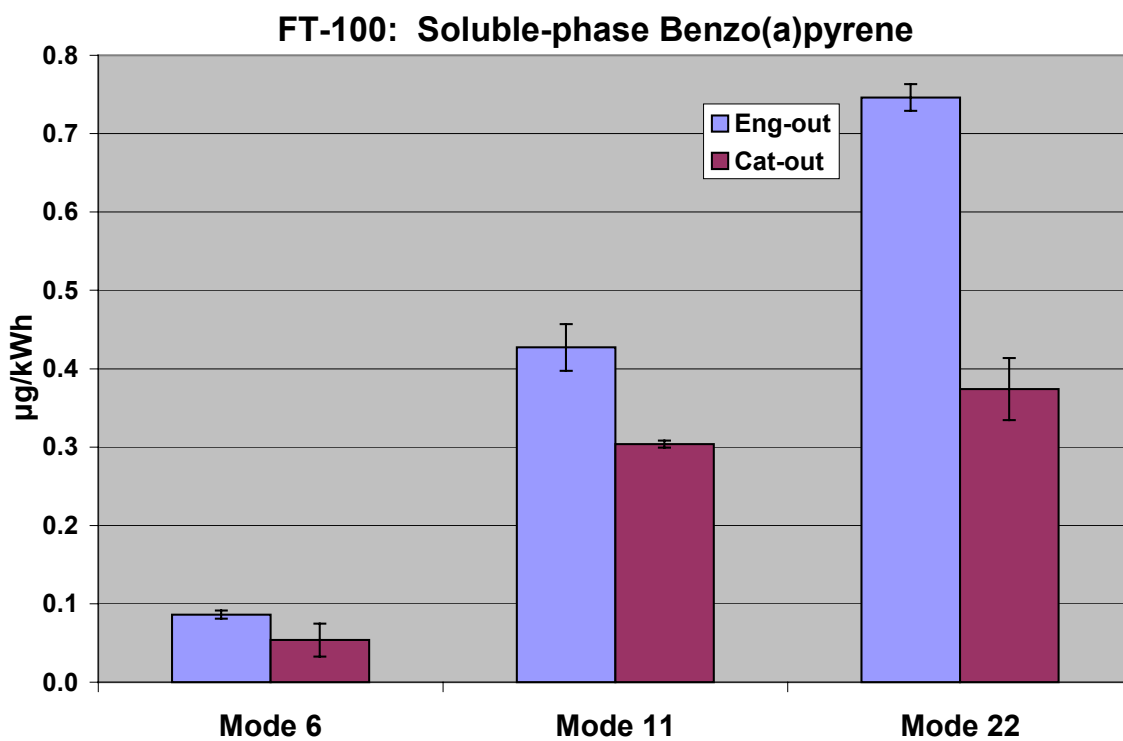


Figure H-32. Soluble-Phase Benzo(a)pyrene Emissions with Fischer-Tropsch Fuel



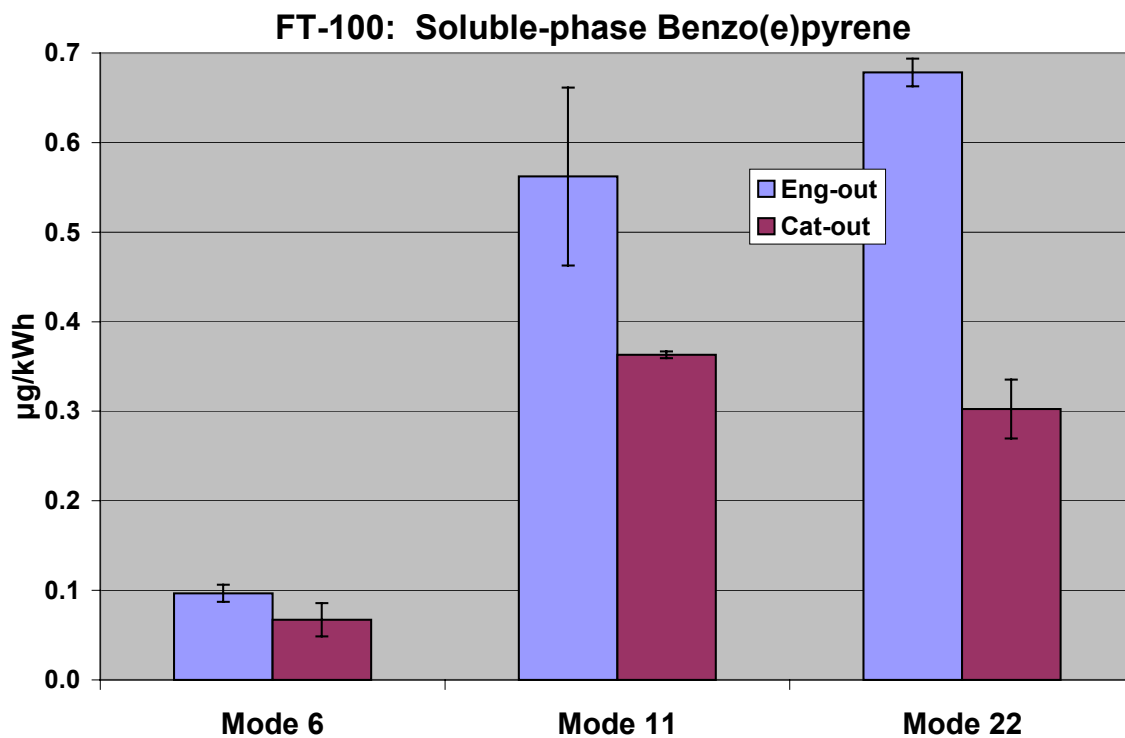


Figure H-33. Soluble-Phase Benzo(e)pyrene Emissions with Fischer-Tropsch Fuel

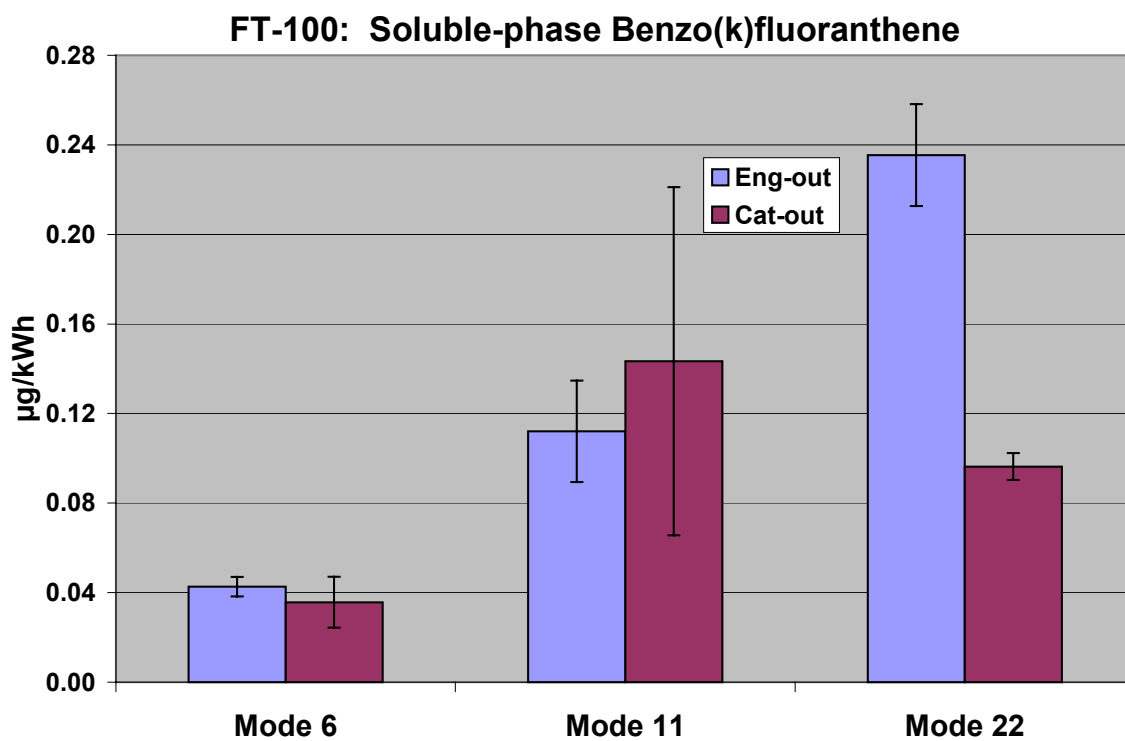


Figure H-34. Soluble-Phase Benzo(k)fluoranthene Emissions with Fischer-Tropsch Fuel

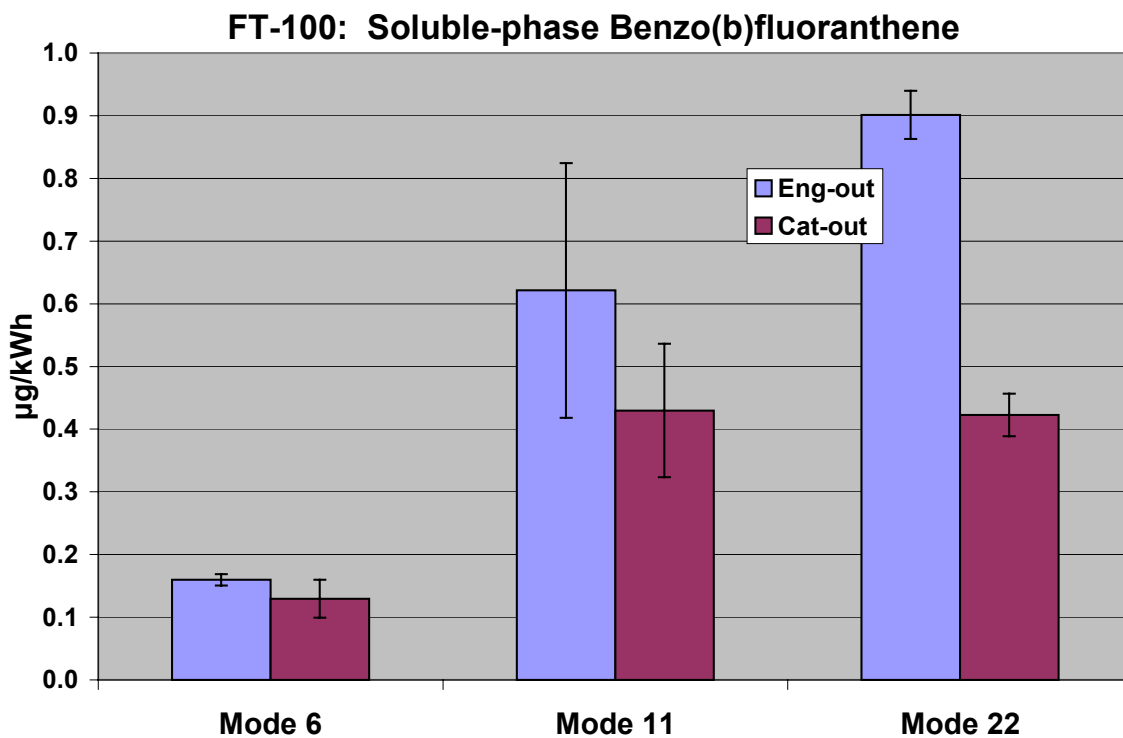


Figure H-35. Soluble-Phase Benzo(b)fluoranthene Emissions with Fischer-Tropsch Fuel

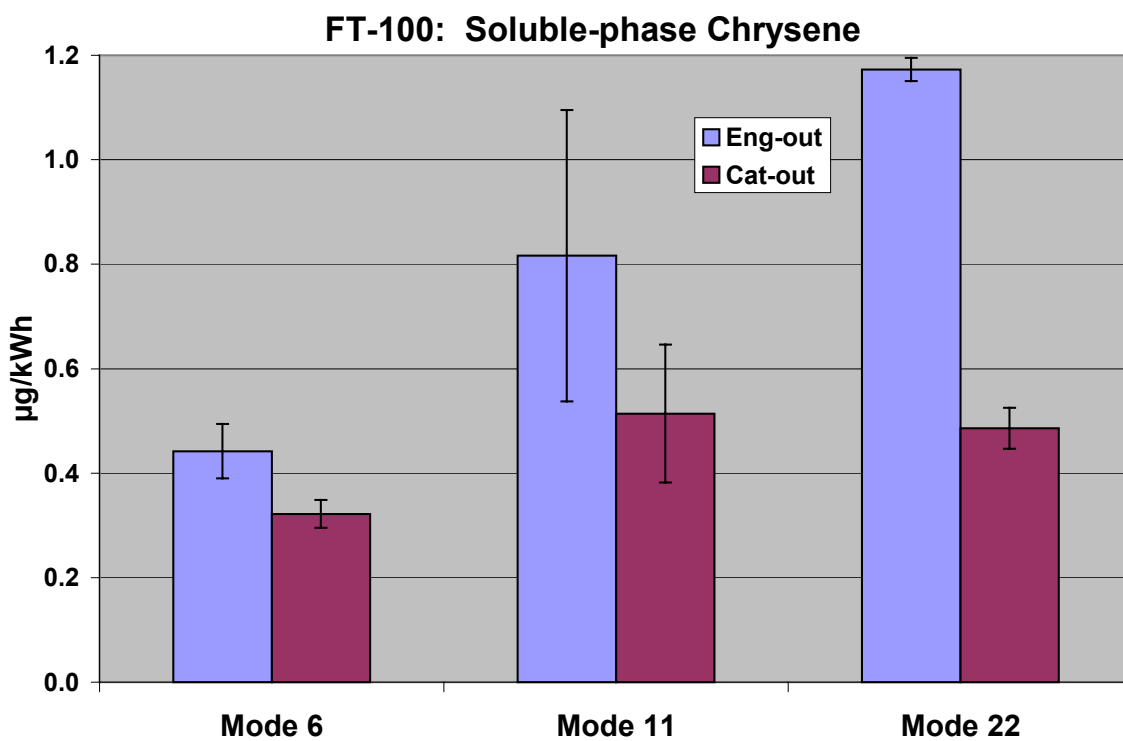


Figure H-36. Soluble-Phase Chrysene Emissions with Fischer-Tropsch Fuel

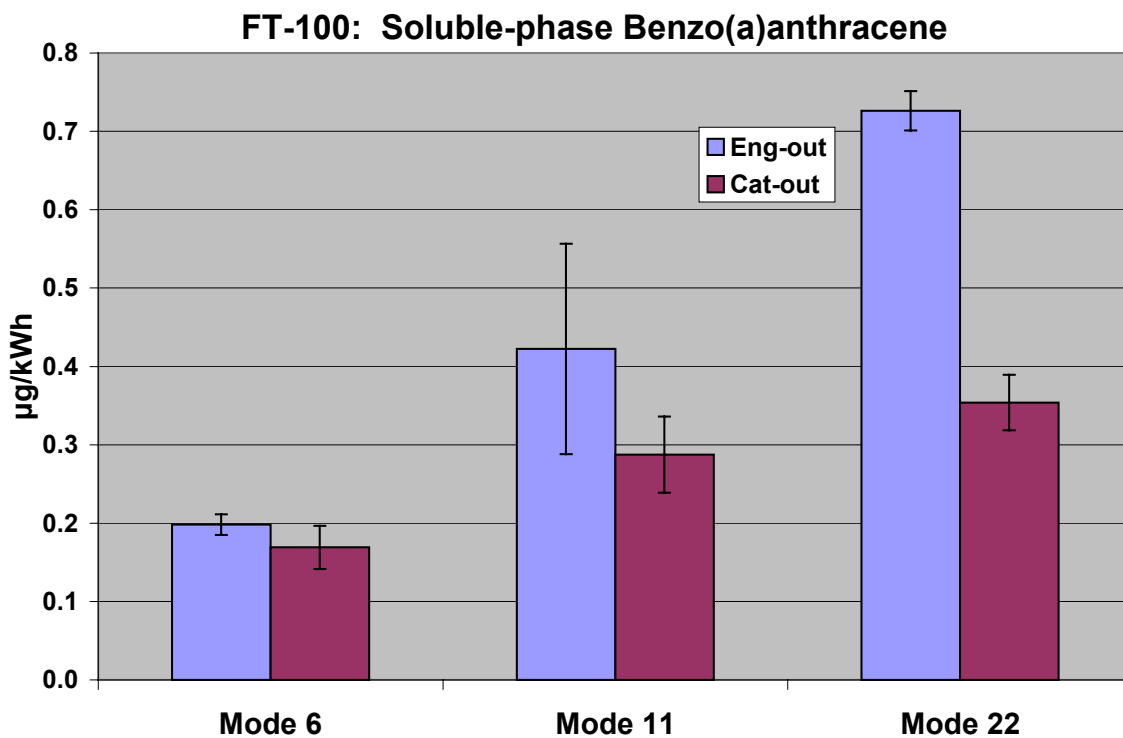


Figure H-37. Soluble-Phase Benzo(a)anthracene Emissions with Fischer-Tropsch Fuel

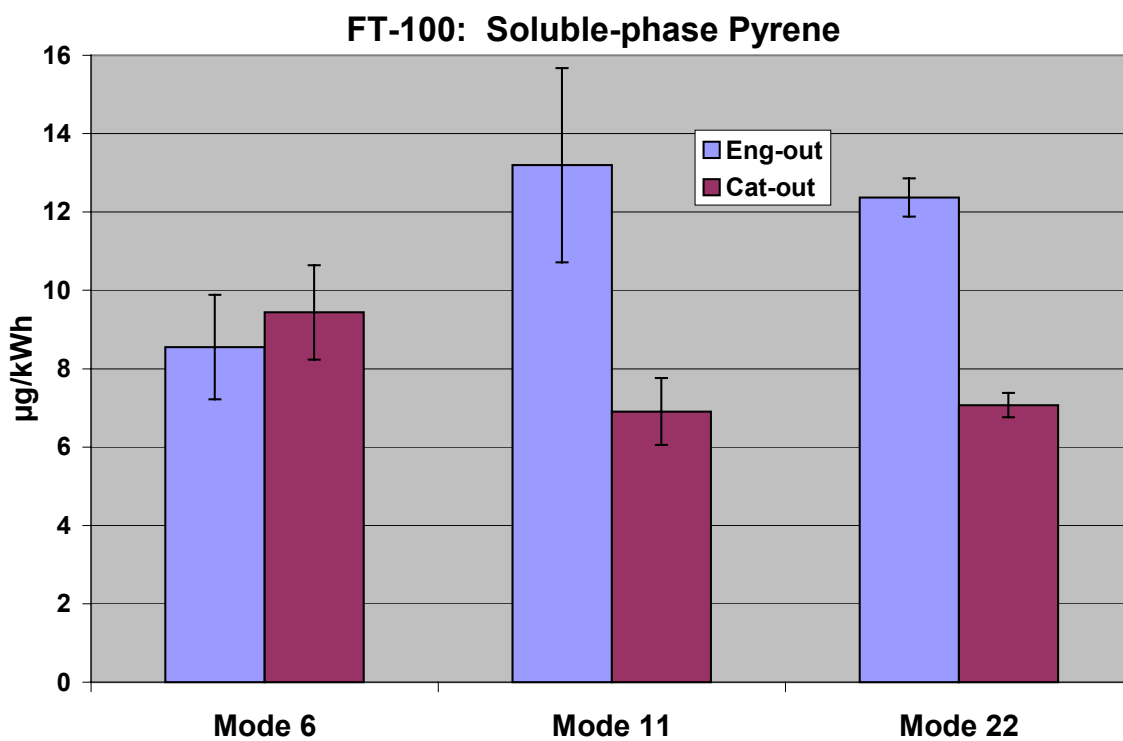


Figure H-38. Soluble-Phase Pyrene Emissions with Fischer-Tropsch Fuel

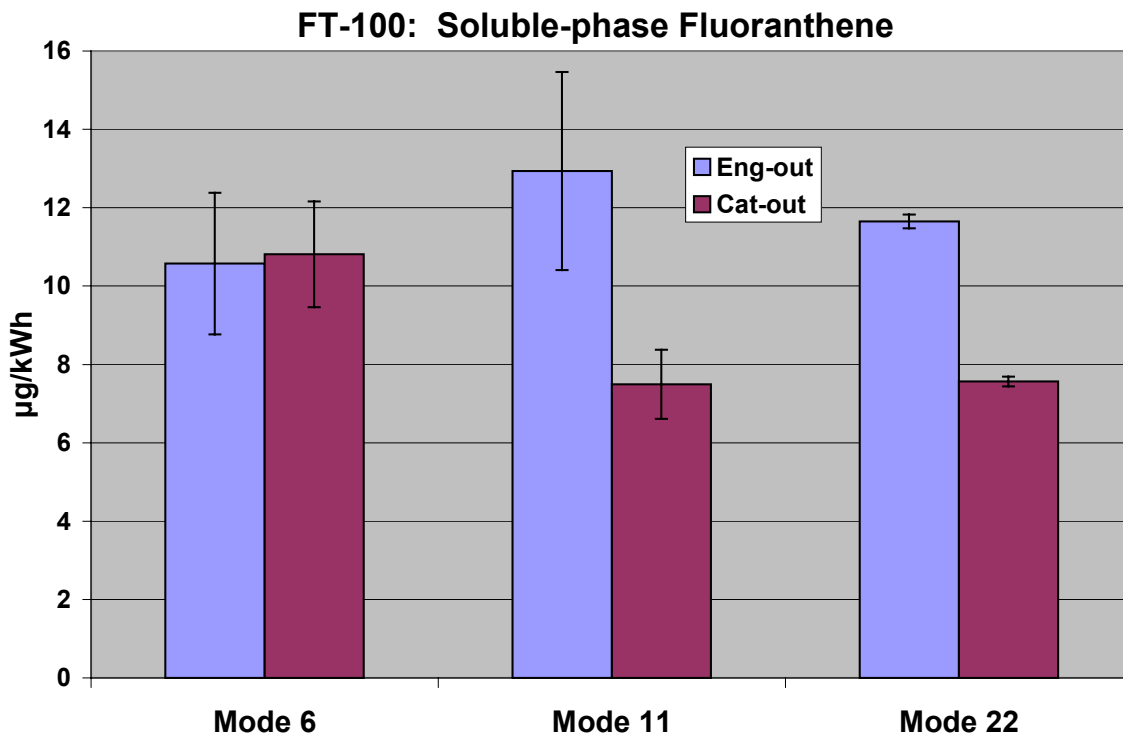


Figure H-39. Soluble-Phase Fluoranthene Emissions with Fischer-Tropsch Fuel

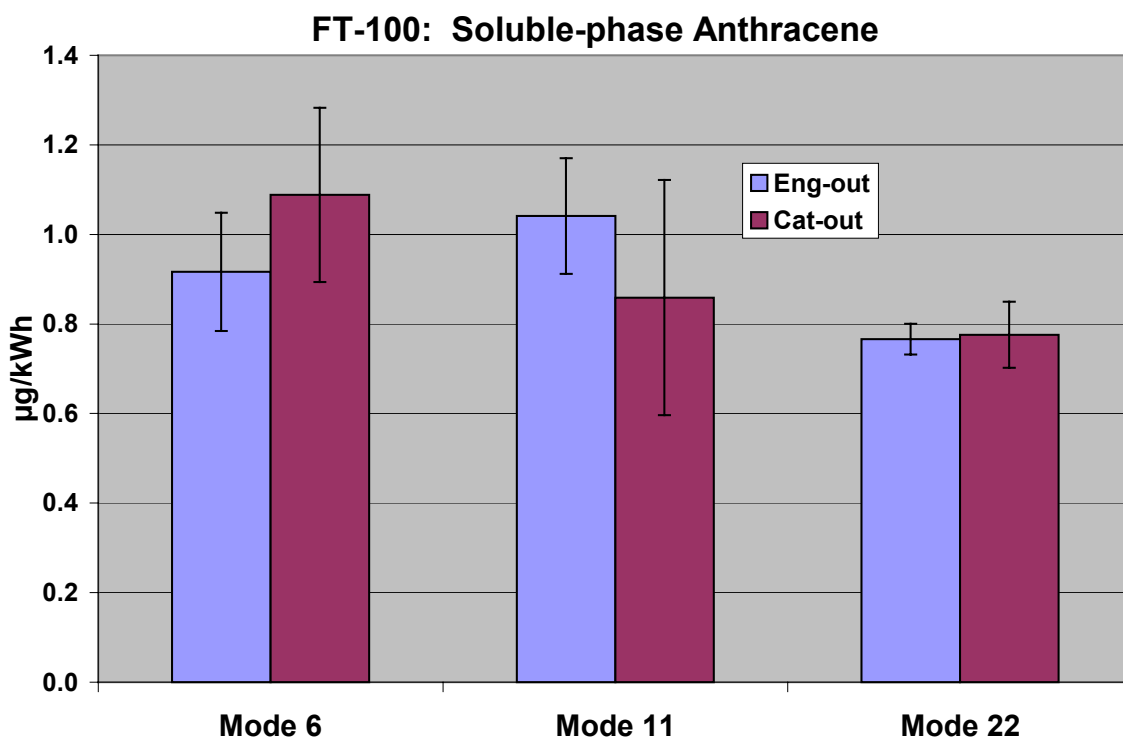


Figure H-40. Soluble-Phase Anthracene Emissions with Fischer-Tropsch Fuel

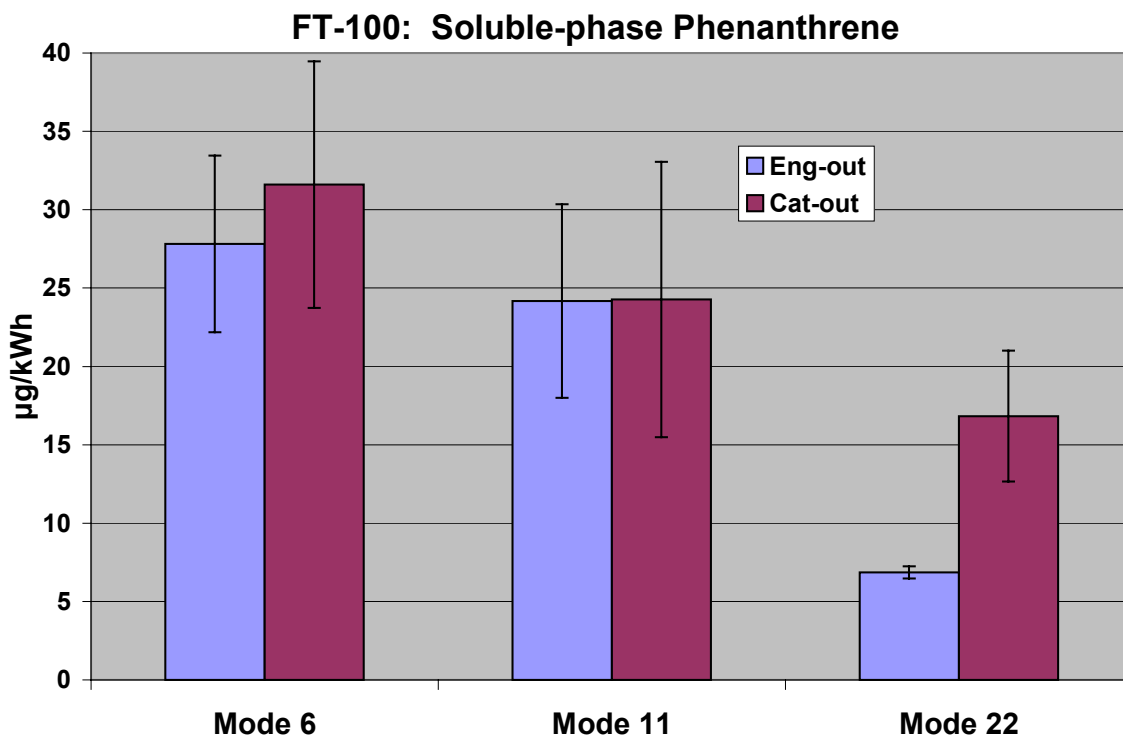


Figure H-41. Soluble-Phase Phenanthrene Emissions with Fischer-Tropsch Fuel

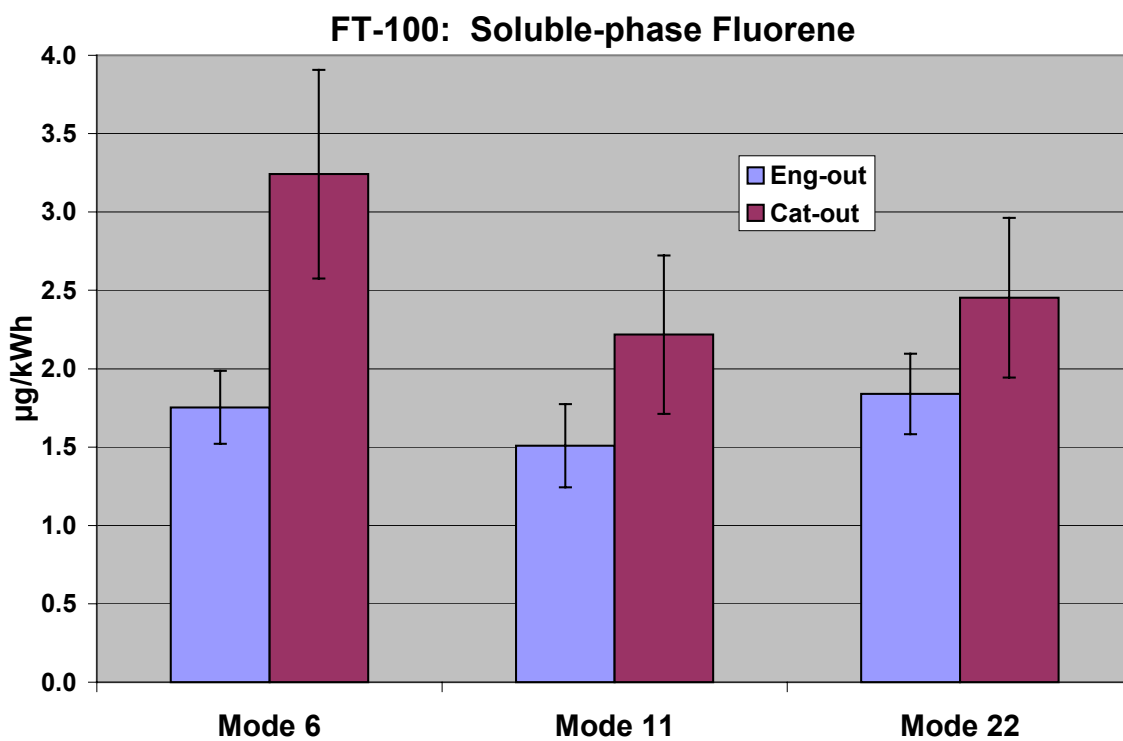


Figure H-42. Soluble-Phase Fluorene Emissions with Fischer-Tropsch Fuel

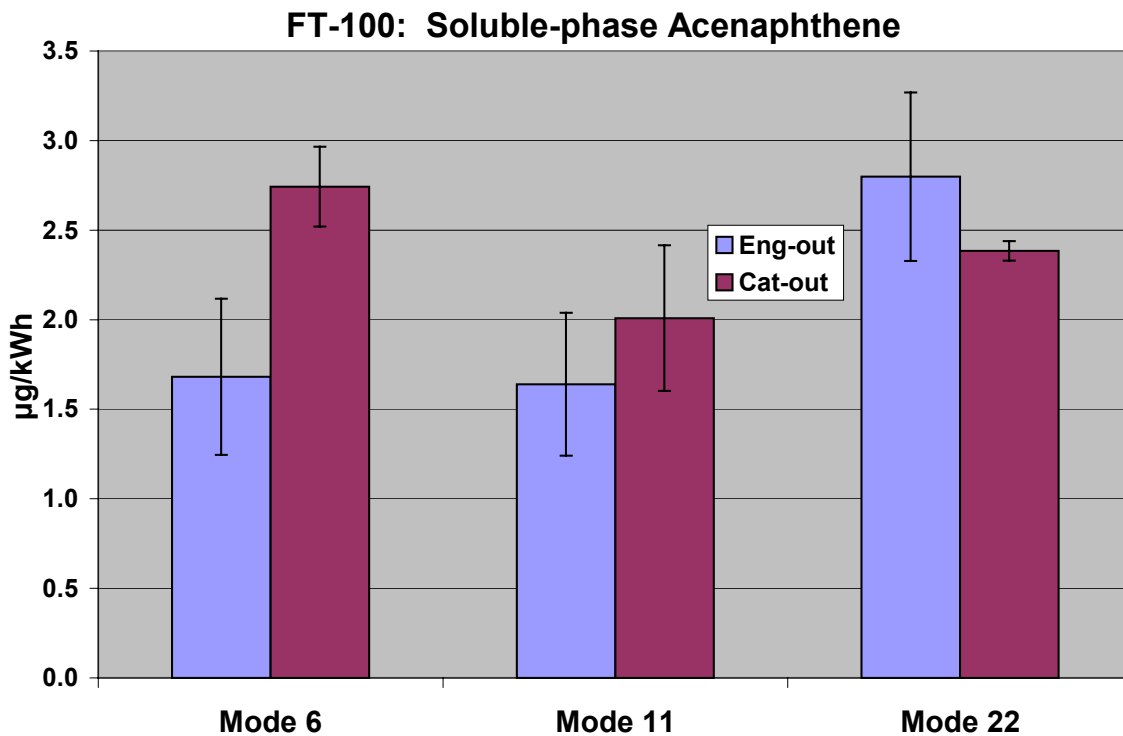


Figure H-43. Soluble-Phase Acenaphthene Emissions with Fischer-Tropsch Fuel

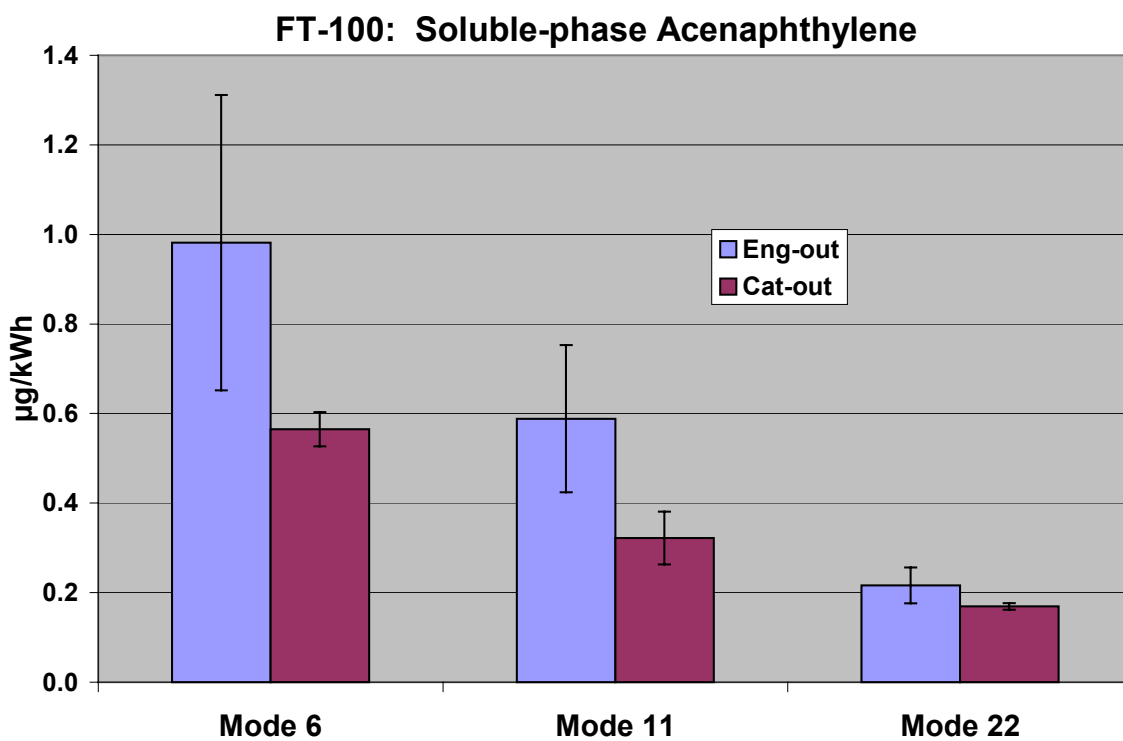


Figure H-44. Soluble-Phase Acenaphthylene Emissions with Fischer-Tropsch Fuel

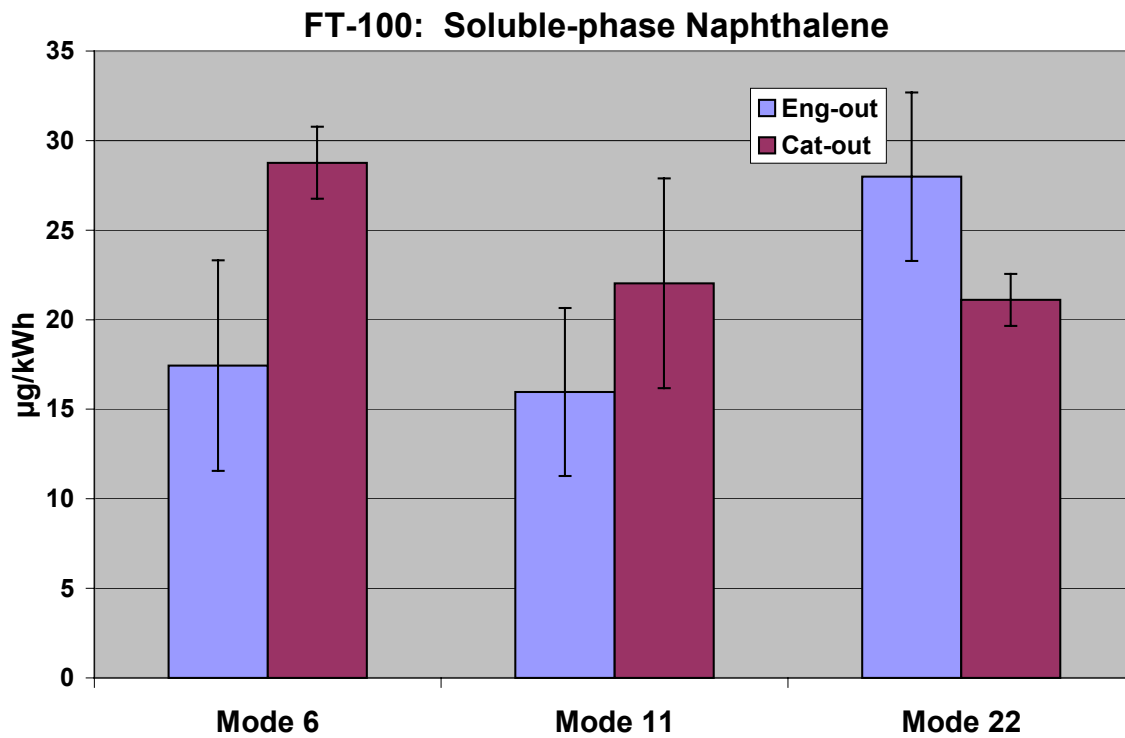


Figure H-45. Soluble-Phase Naphthalene Emissions with Fischer-Tropsch Fuel